XXII International conference on Chemical Reactors
CHEMREACTOR-22

London, UK
September 19-23, 2016

ABSTRACTS

Boreskov Institute of Catalysis of the Siberian Branch
of the Russian Academy of Sciences, Novosibirsk, Russia

University College London, United Kingdom

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Scientific Council on Theoretical Fundamentals of Chemical
Technology RAS Scientific Council on Catalysis RAS

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ABSTRACTS

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The proceedings include the abstracts of plenary lectures, keynote lectures, oral, poster and virtual presentations of the following scientific areas:

- **Section I.** Advances in Chemical Reactor Fundamentals;
- **Section II.** Chemical Reaction Engineering and Reactor Design – Novel Experimental Approaches, Modeling, Scale-Up and Optimization;
- **Section III.** Chemical Reactors and Technologies for Targeted Applications;
- **Section IV.** Advanced Processing of Conventional and Unconventional Hydrocarbon Feedstocks.

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SCIENTIFIC PROGRAM

Advances in Chemical Reactor Fundamentals

Chemical Reaction Kinetics

Energy & Mass Transfer in Chemical Reactors and first principles calculations

Fundamentals of Hydrodynamics and Fluid Flow in Chemical Reactors

Chemical Reaction Engineering and Reactor Design – Novel Experimental Approaches, Modeling, Scale-Up and Optimization

Mathematical Simulation: Multiscale Analytic and Computational Studies of Chemical Reactors

Development of Chemical Reactors and Flow-Sheeting of Reactive Processes

New Chemical Reactor Designs (e.g., Structured Reactors, Membrane Reactors, Microreactors)

Process Intensification and Novel Approaches in Multifunctional Reaction Processes (e.g., Microwave/Induction Heated Reactors, Ultrasonic Reactors, Unsteady-State Forcing and Sorption Enhancement in Chemical Reactors, Multifunctional Reactors, Nature-Inspired Engineering of Reaction Processes, High-gravity, High-Shear Reactors)

Chemical Reactors and Technologies for Targeted Applications

Environmental Protection and Utilization of Waste

Reactors for Polymers and Other Novel Materials with Targeted Properties

Processing of Biomass and Renewable Feedstocks

Electrochemical and Photochemical Reaction Engineering

Engineering and Use of Novel Structured Catalytic Materials

Biochemical Engineering

CO_2 Sequestration and Utilisation

Advanced Processing of Conventional and Unconventional Hydrocarbon Feedstocks

Modern Reactive Technologies for Natural Gas, Oil and Coal Processing

Chemical Processes for Intensification of Fuel Production

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Chemical Reactors and Processes for Treatment of Heavy Hydrocarbon Feedstock and Shale Oil

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CONFERENCE PROCEEDINGS:

CHEMICAL ENGINEERING JOURNAL (*Elsevier*)

CHEMICAL & ENGINEERING PROCESSING: PROCESS INTENSIFICATION (*Elsevier*)

PLENARY LECTURES

A Professor Mikhail Slin'ko Honorary Lecture

ADVANCED FUNDAMENTAL KINETICS FOR HYDROCARBON PRODUCTION AND CONVERSION PROCESSES

Froment G.F.

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The conversion of hydrocarbon fractions or their production out of H_2 and CO/CO_2 involves extremely complex reaction schemes. For a long term chemical engineering has resorted to an approach describing the process in terms of a small number of "lumps", i.e. groups of components with a postulated identical behavior. The approach is questionable. What is the number of required lumps for a reliable performance? Do the components of these lumps really follow the same reaction paths? Are the properties of their components really sufficiently close? Are their rates really identical? What if the real feed composition is modified – do the lumped kinetics of the process then have to be re-determined?

Instead, the present talk deals with an approach that decomposes the process into its detailed network of fundamental elementary steps and that requires in the first place an adequate detailed feed analysis. The rates of the elementary steps are expressed in terms of the "single event kinetics" concept. Thereby, the ratio of the symmetry numbers of the reactant and transition state, which are well documented in the literature, are factored out of the entropy contribution to the rate coefficient. The remaining part of it is unique for a given type of elementary step, whatever the chain length of the reacting species. The enthalpy contribution is formulated according to the Evans-Polanyi relation between the activation energy and the heat of reaction.

The approach is illustrated by means of its application in the formulation of the rate of the Fischer-Tropsch hydrocarbon synthesis and in the hydrocracking of vacuum gas oil.

PL-2

REALIZING VIRTUAL REALITY OF CHEMICAL REACTOR: THE PATH IS AT MESOSCALES

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It is believed that there are two aspects of possible progresses crucial to give rise to a revolutionary changes in chemical engineering: one is physical understanding of mesoscale phenomena at different levels of chemical processes; another is computational capability with sufficient predictability and scalability. Combining these two progresses, the long dream of chemical engineers to realize real-time simulation of chemical processes, that is, virtual reality, could become a real practice. This was just a dream 10 years ago, but now would be probably a reality if sufficient efforts could be made along with this direction.

This presentation reviews the relevant progresses on these two aspects at Institute of Process Engineering, Chinese Academy of Sciences. It is indicated that there are huge potentials in integrating mesoscale understanding and computational capability to realize virtual reality in chemical engineering. Understanding mesoscale phenomena will gives rise not only to good predictability in physical modeling, but also to complete optimization of efficiency of computation, vice versa, computation will be an important tool in understanding mesoscale complexity which is likely not feasible for most of measurement technologies due to the limitation of resolution in both time and space. A demonstration version of virtual reality of gas-solid two-phase systems, based on this mesoscale strategy, will be presented. Challenges in next step of development will be identified. As long as virtual reality becomes a real practice, the capability of chemical engineering will be totally revolutionized! However, traditional thinking mode is not sufficient to lead to this change, and transdisciplinarity is the only path to reach this goal!

BIFURCATIONS IN THE OXIDATIVE COUPLING OF METHANE

**David H. West[1], Sagar Sarsani[2], Vemuri Balakotaiah[3],
Wugeng Liang[2], Huong Nguyen[2]**

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The basic chemicals and plastics industry is built on a simple idea: convert a cheap feedstock into something more valuable. Because of recent trends in oil production, we have seen some interesting changes in feedstock availability and price, which have renewed interest in methane conversion to chemicals. Catalytic oxidative coupling of methane (OCM) has been intensively studied for more than 35 years, but has never been commercialized. Practically every aspect of the problem has been studied: catalyst screening (by high throughput experimentation and more traditional methods), kinetics and mechanism, novel reactors, novel catalytic materials (e.g., monoliths, biotemplated nano-wires, electrospun ceramic nanofibers), theoretical aspects (via molecular modeling), statistical correlation of published data, novel process concepts, and technoeconomics. One aspect that has not been given much attention is the consequences of the highly exothermic nature of the OCM reaction. While Lunsford [1] reported the presence of thermal effects, the phenomenon was not investigated in much detail since. Like other partial oxidations, the OCM reaction is susceptible to thermal effects [2]. We will show that it is important to consider the various bifurcations (e.g., ignitions and extinctions) that occur even when screening catalysts in a typical laboratory experiment.

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PL-4

MAGNETIC RESONANCE STUDIES OF FLUID (MAL)DISTRIBUTION AND HYDRODYNAMICS IN MULTIPHASE REACTORS

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Magnetic Resonance (MR) techniques are now well-established in application to imaging gas, liquid and solid phase distributions inside chemical reactors. Our motivation for applying MR methods to chemical reactors is that both chemical composition and hydrodynamics can be tracked in both space and time. At the highest level, MR methods in chemical reactors are analogous to those used in MRI in hospital environments. Thus, just as we image blood flow and the internal structure of the body, so too we can measure the hydrodynamics and internal 'structure' of reactors. The presentation will include an introduction to what can be measured using MR by means of examples taken from reaction engineering, alongside discussion of where MR 'fits in' to the process tomography landscape and what typical MR hardware looks like and costs.

Examples will be taken from a range of different reactor environments which demonstrate the different types of measurement that MR can make. In many cases, techniques can be developed to enable new measurements required to gain understanding of particular systems. Examples of measurements will be taken from research activities addressing fixed-bed reactors, gas-solid fluidised bed reactors and gas-liquid bubbly flows:

Fixed-Bed Reactors

- Heterogeneity in single-phase flow
- Catalyst wetting during trickle flow and forced pulsing
- Gas-liquid distribution in trickle flow and through the transition to pulsing flow
- Comparison of gas-liquid distributions in co-current downflow and upflow, and counter-current flow
- Tracking reaction in fixed-bed reactors

Gas-Solid Fluidised Bed Reactors

- Imaging of jet formation and shape
- Imaging of gas and solids velocity fields
- Tracking bubble and slug rise velocities, and bubble coalescence

Bubble Columns

- Measurement of liquid hydrodynamics in a gas-liquid bubbly flow
- 'Real-time' analysis of bubble size distributions

PL-5

BIOREACTOR SYSTEMS DESIGN FOR THE PRODUCTION OF BIOFUELS AND BIOPHARMACEUTICALS: REFLECTIONS

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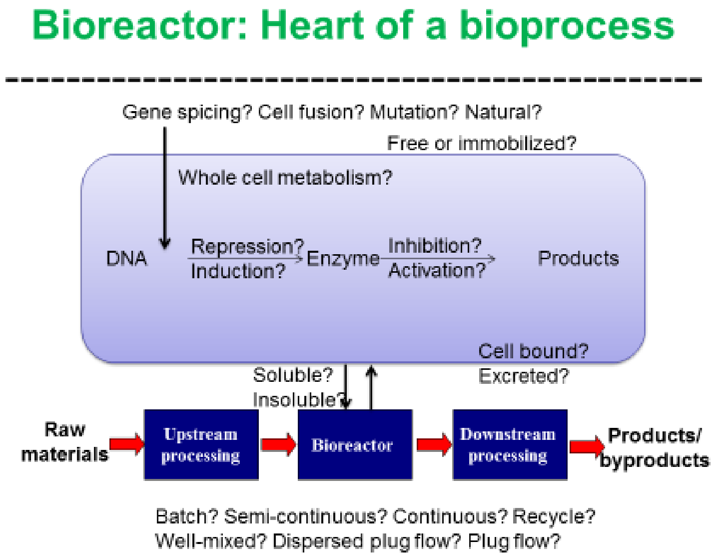
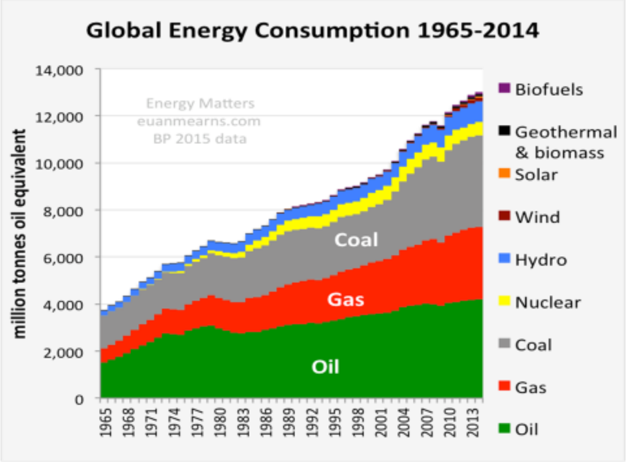
Bioreactors are at the heart of bioprocesses which produce a wide range of value-added products notably biopharmaceuticals, biofuels, and fine chemicals [1]. Based on biotechnology, these bioprocesses are of global socio-economic importance given concerns about healthcare and environmental issues. With this background, the review will highlight the bio-engineering aspects of bioreactor systems design followed by its applications to bio-manufacturing with examples of our studies in biopharmaceuticals [2, 3, 4, 5] and biofuels [6, 7]. The increasing prerequisite impact of the life sciences is noted.

The basic three constituent operational stages in a bioprocess design will be reviewed: upstream operations for preparation of a biocatalyst; midstream operations of the bioreactor for cell cultivation and bioconversion; and downstream operations for recovery and purification of the product. Depending on the bioprocess objective, any of the components could present techno-economic bottlenecks which usually require a multidisciplinary solution based on the biological sciences and engineering strategies. The challenges in the complex interactions between strain engineering and bioprocess engineering are illustrated in the diagram below.



To promote appropriate mass and heat transfer in the multiphase bioreactor, there are several geometric configurations in which the required fluid mixing is driven by mechanical stirrers and/or pneumatic bubbling or waves. Various innovations have been developed for stirrer types and air-lift and wave devices based on transport phenomena considerations. The established engineering correlations can have an overridingly important effect on the bioreactor performance. Challenges are encountered with genetically-unstable host cells and viscous pseudo-plastic fermentation culture broths as examples.

The energy-environment enigma over energy security vs clean environment will be addressed. Within the current climate-change geopolitical debates, there are dilemmas to be examined. The international efforts to develop renewable energy with biofuels have been an ongoing major disappointment as indicated in the diagram below. Remedies are suggested in the adage that “prevention is better than cure”.



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PL-6

ENGINEERING OF AEROSOL REACTORS: SUB-NANO Pd CLUSTERS ON TiO_2 FOR SOLAR-LIGHT REMOVAL OF NO

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The lecture starts with the fascinating history of aerosol reactors from ink production in ancient China to the Bible printing by Gutenberg and to the manufacture of optical fibers, carbon blacks, pigments, fumed silica and filamentary nickel today[1]. The 7 advantages of aerosol reactors over wet-chemistry technologies for material synthesis are presented. Flame aerosol reactors are emphasized for their proven scalability as they dominate both by value and volume the world-wide production of aerosol-made materials today[2]. The early development of these reactors was rather Edisonian but valiant engineering research led to the current particle manufacturing lines of up to 25 t/h. Recent advances in aerosol and combustion sciences have placed aerosol reactor engineering on a firm scientific basis[3] resulting in an array of product compositions way beyond the above ones and impacting catalysis, gas sensing and biomaterials.

Key concepts that greatly facilitate multi-scale aerosol reactor design are[3]: a) the high temperature particle residence time (HTPRT), b) the self-preserving particle size distribution and c) the fractal-like particle structure[4]. From a ChE point of view, aerosol processes offer distinct advantages in large-scale synthesis (tons/hr) of materials, facilitate particle handling and the formation of materials of high purity (e.g. optical fibers) with unique morphology and can even form metastable phases (e.g. low temperature $BaCO_3$ for NOx storage-reduction catalysts). Furthermore, they allow more rigorous process design than in liquid-phase production of particles. So they easily form mixed oxides, salts and even pure metals and highly porous but stable films resulting in novel catalysts, micropatterned sensors for breath analysis, phosphors and bone & dental prosthetics and even nutritional supplements[2]. This has led to synthesis and sales of new materials (e.g. magnetic nanoparticles for nanofluids) and construction of pilot scale facilities by catalyst manufactures (e.g. Johnson Matthey).

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Aerosol-made materials consist typically of clusters of primary particles (PPs) that are formed by chemical reactions in the gas-phase or onto the particle surface and grow further by sintering or coalescence and coagulation. Depending on concentration and HTPRT, either aggregates (PPs held together by strong chemical bonds) and/or agglomerates (PPs held together by rather weak, physical forces) are formed. The former are attractive in catalysis, lightguide preforms and electronics while the latter in nanocomposites, pigments and liquid suspensions[2]. So renewed emphasis is placed on understanding formation and structure of aggregates and agglomerates[4]. For example, primary particles in an aggregate can have a narrower size distribution than that predicted by self-preserving theory[5] as confirmed experimentally at Cabot[6].

In the last part of the lecture and as time permits the above understanding would be exemplified in catalysis showing how controlled synthesis of sub-nano metal clusters on ceramic supports can lead to enhanced catalyst performance with minimal use of noble metals. So Pd clusters onto nanostructured TiO_2 particles are prepared in one step while controlling the Pd cluster size from a few nanometers down to that of single atoms. Under solar light irradiation, these materials remove NOx 3 or 7 times faster than commercial TiO_2 (P25, Evonik) with or without, respectively, photo-deposited Pd on it[7]. Annealing such materials leads to solar photocatalytic NOx removal in a standard ISO reactor up to 10 times faster than that of commercial TiO_2. Such superior performance can be attained by only 0.1 wt % Pd loading on TiO_2. Annealing these flame-made powders decreases the amorphous TiO_2 fraction and increases its crystal and particle sizes while single Pd atoms and clusters are stable up to, at least, 600 °C for 2 hours in air but at 800 °C they grow into PdO nanoparticles whose fraction is comparable with the nominal Pd loading proving the presence of Pd atoms on the catalysts surface along with STEM analysis. Diffuse Reflectance Infrared Fourier Transform Spectroscopy reveals NO adsorption on single, double, 3- and 4-fold coordinated Pd atoms depending on their flame concentration and annealing conditions. The peak intensity of NO adsorption sites involving multiple Pd atoms is substantially lower in TiO_2 with 0.1 than 1 wt % Pd but that intensity from single Pd atoms is comparable. This indicates the dominance of isolated Pd atoms compared to their clusters in Pd/TiO_2 containing 0.1 wt % Pd that match or exceed the photocatalytic NOx removal at higher Pd contents proving the potential of flame-depositing of Pd atoms.

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KEYNOTE LECTURES

ACCURATE AND EFFICIENT COMPUTATIONAL FRAMEWORKS FOR REACTION KINETICS: TOWARD FIRST-PRINCIPLES BASED REACTOR DESIGN

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Modelling catalytic kinetics is indispensable for the design of reactors and chemical processes. However, developing accurate and computationally efficient kinetic models remains challenging. Empirical kinetics models often applied in the design of reactors, incorporate assumptions about rate-limiting steps and may thus not be applicable to operating regimes far from those where they were derived. Detailed microkinetic modelling approaches overcome this issue by taking into account (at least in principle) all elementary steps of a reaction mechanism. However, the majority of such kinetic models employ mean-field approximations and are formulated as ordinary differential equations, which leads to an approximate description of catalytic kinetics by omitting spatial correlations. On the other hand, kinetic Monte Carlo (KMC) approaches provide a discrete-space continuous-time stochastic formulation that enables a detailed treatment of spatial correlations in the adlayer (resulting for instance from adsorbate-adsorbate lateral interactions), but at a significant computation expense [1, 2].

Motivated by these challenges, in the first part of this talk we discuss the necessity of KMC descriptions that incorporate detailed models of lateral interactions. Focusing on a titration experiment involving the oxidation of pre-adsorbed O by CO gas on Pd(111), we discuss experimental findings that show first order kinetics at low temperature (190 K) and half order kinetics at high temperature (320 K), the latter attributed to island formation in the original experimental work [3]. We employ detailed KMC modelling in which the effect of coverage on the reaction barrier is captured by cluster expansion Hamiltonians and Brønsted-Evans-Polanyi (BEP) relations [4]. By quantifying the effect of adlayer structure versus coverage effects on the observed kinetics, we rationalise the experimentally observed kinetics. Our calculations show that it is coverage effects which lead to the half order kinetics at 320 K, rather than O-island formation as previously thought [5, 6].

In the second part of the talk, we discuss our ongoing work in the development of approximations that take into account such coverage effects but are much more computationally efficient than KMC, making it possible to use such models in reactor design. We focus on a model for NO oxidation incorporating first nearest neighbour lateral interactions and construct a sequence of approximate models of progressively higher accuracy, starting from the mean-field treatment and continuing with a sequence of Bethe-Peierls models with increasing cluster sizes. By comparing the turnover frequencies of these models with those obtained from KMC simulation, we show that the mean-field predictions deviate by several orders of magnitude from the KMC simulation results, whereas the Bethe-Peierls models exhibit progressively higher accuracy as the size of the explicitly treated cluster increases. While more computationally intense than mean-field, these models still enable significant computational savings compared to a KMC simulation, thereby paving the road for employing them in multiscale modelling frameworks.

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MULTISCALE MODELING OF REACTION AND DIFFUSION WITH IMPACTS ON CHEMICAL REACTOR ANALYSIS AND DESIGN

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There is a clear hierarchy in models used for simulations, ranging from detailed (relativistic) quantum dynamics of particles, via a cascade of approximations, to the macroscopic behavior of complex systems [1]. A particular multiscale approach from reactions at the active sites, multicomponent adsorption and diffusion processes inside pores, via the full pellet to the reaction will be presented [2-5]. On the reaction level DFT, MP2, CCSD(T) and transition state theory are used. Multicomponent adsorption and diffusion are simulated by Monte Carlo (MC) and Molecular Dynamics (MD) approaches in the grand canonical ensemble. To keep the caluclations feasible, linker theories are employed, like ideal adsorption solution theory (IAST) and Maxwell-Stefan equations. A particular attention will be directed towards engineering implications. On the pellet scale the optimization of pore structures will be discussed [6-9]. The performance index is the minimum yield of a desired product or the maximum operating time for supports with changing pore structure owing to depositions, for example hydrodemetallation. Subsequently, problems of diffusion path lengths reduction in reactors and its possibilities in process intensification will be investigated [10]. Convective forced flow inside membranes allows to control residence time inside pores. The pore size distribution is taken to be quite large to keep the pressure drop on a low level. This reactor is particularly useful for consecutive reactions. Catalytic pervaporation of 4-chlorophenol in PEBA membrane will be another example. Intensification of gas/liquid transport will be demonstrated by the example of a vibrating bubble column [11], spinning disc reactor, and monolitic loop reactor [12]. Reduction of diffusion path lengths and intensification of mass and heat transport can be achieved by means of microreactors [13]. Its pros and cons will be discussed [14]. Some reactions can be accelerated by ultrasound [15]. Calculation of sound fields in reactors will be mentioned, and an example of an enzyme reaction will be presented.

KL-2

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SYNTHESIS OF NANOSTRUCTURED MATERIALS IN FLUIDIZED BED REACTORS

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Core-shell nanoparticles and other nanostructured particles have high potential in applications such as catalysis, energy storage and pharma. However, a hurdle in their utilisation is that typically large amounts of such materials are required. Current liquid-phase and gas-phase synthesis methods often lack the high precision required or do not lend themselves to large-scale production. Gas-phase coating using atomic layer deposition (ALD, a variant of chemical vapour deposition) can be used to provide the surface of a particle with either an ultrathin continuous coating or a decoration of nanoclusters. When carried out in a so-called fluidized bed, ALD is an attractive way of producing nanostructured particles with excellent scale-up potential. In such a system, the particles are suspended in an upward gas flow. We can do this both for nanoparticles and micron-sized particles. Nanoparticles – contrary to what is typically observed for larger particles – are fluidized as very dilute agglomerates with distinctive fluidization characteristics. I will discuss the challenges related to fluidization and coating of nanoparticles. Moreover, I will give a number of examples of the applications of nanostructured particles.

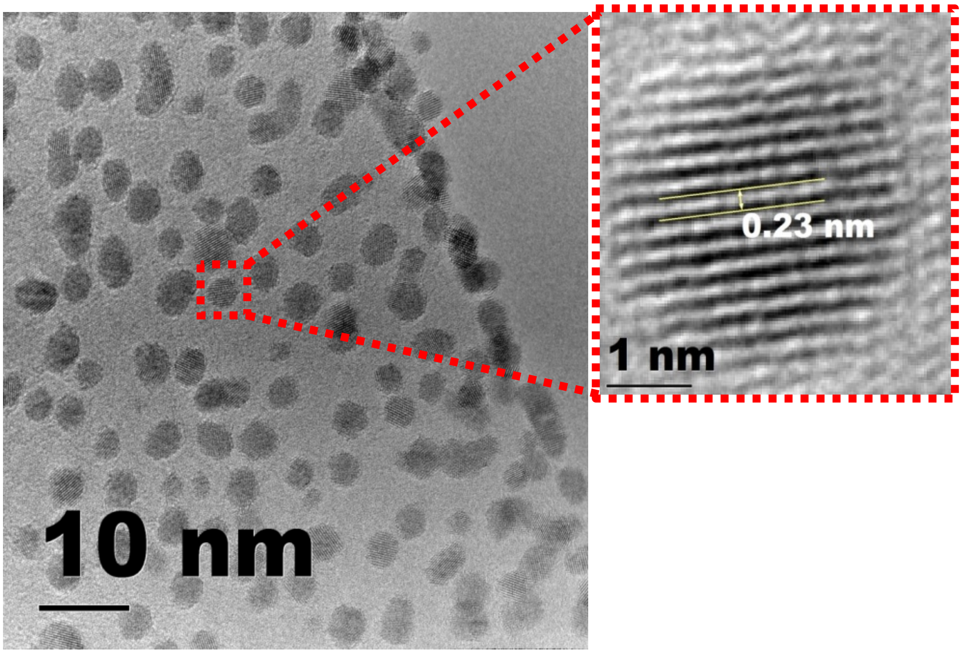

Figure. Platinum nanoclusters deposited on graphene using atomic layer deposition. The zoom-in shows the metallic nature of the nanocluster

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’UNMIXED REACTIONS’ – HOW TO EXPLOIT PERIODICALLY-OPERATED AND MEMBRANE REACTORS

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Reversible reactions (and irreversible reactions without a single product) require a product separation step. Such separation steps are often costly and lead to process inefficiencies. Here we discuss the possibilities and challenges of using ‘unmixed reactions’ where individual reactants are never mixed thus reducing or even eliminating the need for separation. Unmixed reactions require either the spatial separation of process streams (using e.g. membranes with permselectivity for a reaction intermediate) or the temporal separation of process streams using dynamic processes and materials that can periodically store (a carrier material) a reaction intermediate. After discussing general considerations for unmixed reactions this presentation will focus on materials design for a range of applications.

Membranes and membrane reactors are of great interest in the chemical industries because they offer the possibility of improved yields and more compact plant. Clearly the availability of membrane systems having suitable performance at an acceptable cost is an important consideration. Organic membranes can be difficult to use at high temperatures, while porous inorganic membranes tend to have problems associated with selectivity. We will focus on the use of inorganic, dense, ion-conducting membranes. Such membranes can be highly selective. We will explore their use in new membrane-based chemical process applications. Mixed ionic and electronic (MIEC) conducting metal oxides can be employed as oxygen permeable membranes (in the case of coupled oxygen ion and electron transport) or hydrogen permeable membranes (in the case of coupled proton and electron transport). Dual ion conducting membranes are defined as membranes in which there are two ionic charge carriers. Such membranes may be single phase or dual phase. If a porous oxide ion conductor is infiltrated with a molten carbonate salt a dual phase dual ion conducting membrane is formed. For example, carbon dioxide permeation is due to the counter diffusion of carbonate ions and oxygen ions. Under an oxygen chemical potential difference an oxygen permeable ceramic membrane can supply pure oxygen to a hydrocarbon for e.g. partial oxidation. This permits the use of air as the oxidant (as nitrogen is not introduced into the hydrocarbon stream) and can lead to more intensified, efficient hydrocarbon processing. Other novel process routes involve hydrogen production, internal reforming within a solid oxide fuel cell and carbon dioxide capture.

Chemical looping involves a sequence of cyclic reactions and e.g. a solid carrier material to store and release a reaction intermediate. Theoretically, the carrier at the end of the cycle will remain unchanged whilst the products from the reduction and the oxidation step are separated. For example, iron oxide can be used as an oxygen carrier material (OCM) for hydrogen production from the water-gas shift reaction. However, although iron oxide shows significant usable oxygen capacity for this reaction, it loses its activity rapidly due to sintering and agglomeration. Perovskites, such as $La_{0.7}Sr_{0.3}FeO_{3-\delta}$, have been proposed as alternative oxygen carrier materials due to their high stability and stable productivity under long term redox cycles. They are also oxygen ion-conducting MIECs allowing rapid oxygen permeation through their structure. However, the small oxygen capacity of perovskites results in less hydrogen production per cycle than with iron oxide. Here we show how composite OCMs can be designed to achieve high stability and capacity where iron oxide clusters are embedded in an $La_{0.7}Sr_{0.3}FeO_{3-\delta}$ perovskite matrix. The hydrogen productivity and the stability of the composite OCMs is analysed using a micro-reactor fed with carbon monoxide and water alternatively to produce carbon dioxide and hydrogen in separate streams. More that two hundred redox cycles are performed.

Parallels will also be drawn between membrane and chemical looping processes. We will show that any chemical looping process has a membrane analogue and vice versa.

REDUCTION OF DIESEL ENGINE NO_X EMISSIONS BY FAST PERIODIC PULSING

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Introduction

Current technologies to reduce NOx emission from diesel and lean burn vehicles are selective catalytic reduction (SCR) and NOx storage and reduction (NSR). NSR is more practical for light-duty passenger cars because SCR is cost prohibitive. NSR involves cyclic operation over a lean NOx trap (LNT) catalyst, which stores NOx under lean feed, followed by regeneration by a short rich feed purge containing a mix of CO, H_2 and hydrocarbons (HC). At low regeneration temperature NSR suffers from inefficient reductant utilization and undesired byproduct formation (N_2O, NH_3). At high temperature its performance is poor due to decreased NOx storage capacity. Toyota researchers reported enhanced high temperature NOx conversion during NSR conducted at much faster cycling [1]. Our recent findings support Toyota's claim of a new mechanism for selective NOx reduction involving selective conversion of adsorbed intermediates [2-4]. The experiments reveal notable non-isothermal behavior that contributes to the conversion enhancement as well as enhancement at much lower feed temperatures, conditions for which conventional NSR is ineffective. To date, there have been few reports of the effect of hydrocarbon reductant type or of modeling efforts to corroborate fast cycling experiments. The objective of this continuing study is to corroborate the measurements with a comprehensive model, to provide insight, and to guide optimization efforts.

Results and Discussion

Monolithic LNT catalysts contain $Pt/Rh/BaO/CeO_2/Al_2O_3$ with a washcoat loading of 4.6 g/in^3 and PGM loadings between of 90 and 120 g/ft^3 cylindrical monoliths (~55 channels, D = 0.42 in, L = 1 in). A four-way switching valve generated the high-frequency HC pulsing via fast switching between lean and rich feed. Reductants were injected at different frequencies and concentrations into a lean NO feed at a space velocity of ~75k h^{-1} and cycle spanning 60s lean/10 s rich to 6s lean/1s rich. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used on catalyst powders to identify surface species.

Experiments for a range of feeds and cycle timing reveal interesting dynamical features and NOx conversion enhancement over a wide range of feed temperatures. The results reveal that H_2 and propene respectively result in moderate and high conversion enhancement for shorter cycle times, while propane leads to negative results. Thus the reactivity of the reductant plays an important role in fast cycling NSR. DRIFTS measurements of model LNT catalysts provide evidence for an array of intermediates, including isocyanates, aldehydes, oximes, etc. when using propylene. The performance is enhanced by ceria, possibly through the spillover of oxygen to the precious metal crystallites and/or direct involvement in the NOx reduction.

A 1+1 D monolith reactor model including the relevant transport processes was combined with a phenomenological reaction network that builds on the NSR model of Shakya et al. [5]. The network includes the generation of an olefinic surface isocyanate from propylene oxidation, following clues from DRIFTS, which under fast cycling conditions is predicted to be the preferred pathway for NOx reduction. The model reveals an interesting interplay between the generation of the surface species and the N_2 selectivity as a function of the cycle frequency. When H_2 is the reductant the moderate enhancement is the result of eliminating NOx breakthrough during the storage step. When propylene is the reductant the model predicts a switch from the classic NSR pathway at slow during the 70 s period cycling to the surface intermediate pathway during 7 s period cycling. Significant nonisothermal behavior is predicted which has a notable effect on the catalyst performance. These and other simulations provide insight into the complex fast cycling NOx storage and reduction.

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EVALUATING THE POTENTIAL OF FORCED PERIODIC OPERATIONS OF CHEMICAL REACTORS - THE NONLINEAR FREQUENCY RESPONSE APPROACH

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One way to achieve process intensification is to operate the process in a periodic way, by cycling one or more input variables, in order to obtain better average performance compared to the optimal steady-state operation. The source of the possible improvement lies in the process nonlinearity. Nevertheless, the improvement is obtained only in some cases, while in some others the periodic operation can result in deterioration.

Periodic operations of chemical reactors have been attracting attention of a number of research groups, since the pioneering works of, e.g., Douglas and Rippin [1] and Bailey [2]. A review of the recent research in this area can be found in a book by Silveston and Hudgins [3].

Testing whether a potential periodic process is favourable or unfavourable generally demands long and tedious experimental and/or numerical work. In this work we present an alternative approach, based on the nonlinear frequency response (NFR) analysis, which gives an approximate value of the average process performance directly, without numerical simulation. The method is applicable for stable, weakly nonlinear systems.

The mathematical foundations of the nonlinear frequency response method are based on Volterra series and the resulting concept of higher order frequency response functions (FRFs). The method is based on the following facts:

- Frequency response (periodic steady-state) of a weakly nonlinear system consists of a non-periodic (DC) term, the basic and indefinite number of higher harmonics, where only the non-periodic term is responsible for the average process performance during the periodic process.
- The nonlinear model of a weakly nonlinear system can be replaced with an indefinite sequence of frequency response functions of different orders.

- The non-periodic term of the frequency response can be approximated by its dominant term which is proportional to the asymmetrical second order FRF.

The nonlinear frequency response method has been applied for analysis of periodic operations of isothermal and non-isothermal CSTRs with simple reaction mechanisms. Modulation strategies with one modulated input and with simultaneous modulation of two inputs have been analysed. Periodic operations with sinusoidal or any other shape of periodic modulation can be considered. The NFR method gives answers to the following questions:

- Is it possible to improve the performance of a particular reactor by periodic modulation of one or more inputs?
- Which range of frequencies of the input modulation(s) should be used in order to get the improvement?
- If simultaneous modulation of two inputs is used, what is the optimal phase difference between them?
- Are there some optimal values of the input amplitudes that should be used, and if there are, how to determine them?
- What is the approximate extent of the performance improvement for a particular periodic operation, for a chosen set of forcing parameters (frequency, amplitude(s) and phase difference).

The purpose of the method is fast evaluation of periodic operations, with the aim of selecting the cases and conditions which have a potential for improvement and are, therefore, worth of further, detailed numerical and experimental investigation.

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RECENT ADVANCES IN THERMALLY CONDUCTIVE MICROSTRUCTURED CATALYSTS

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The first part of this presentation will focus on conductive honeycomb monolith catalysts. We have shown in the past that there is potential for significant enhancement of radial heat transfer rates in technical multitubular fixed-bed reactors with external cooling if the random packings of catalyst pellets are replaced by structured catalysts with highly conductive honeycomb supports. Indeed, the adoption of multitubular reactors loaded with catalysts coated onto highly conductive honeycomb substrates [1] provides an alternative to conventional packed-bed reactors in order to approach the ideal plug-flow behaviour while (i) enabling isothermal operation of highly endo- and exo-thermic reactions, (ii) facilitating internal mass- transfer, and (iii) limiting pressure drop. This concept has been proposed on the basis of simulation studies [2], confirmed by heat transfer and reactive experiments at the lab scale [3], and first demonstrated in a proof-of-concept campaign of o-xylene oxidation runs (c/o Polynt, Italy) in a single-tube pilot reactor (i.d. = 24.6 mm) loaded with washcoated (V_2O_5/TiO_2) monolithic catalysts with Al honeycomb supports (Corning Inc., USA) operated at typical industrial conditions for PA (phthalic anhydride) production [4]. Herein we specifically illustrate related experimental and modeling activities within a recent project for the development of compact GTL installations, where a major issue is the control of the large Fischer-Tropsch (FTS) reaction heat [5, 6].

The second part of the presentation deals with the study of conductive open-celled foams (or sponges) as potentially enhanced catalyst supports. Recent experimental and modelling results concerning the overall (non-adiabatic) heat transfer performances of metallic foams with different geometrical (porosity, ppi) and structural (FeCrAlloy, aluminium) properties will be illustrated [7,8], pointing out the crucial contribution of heat conduction in the thermally connected sponge matrix.

Based on a detailed modeling analysis, such results will be applied to discuss the potential of highly conductive structured reactors for the methanol synthesis in comparison to the behavior of existing industrial packed-bed reactors [9]. We conclude that conductive structured catalysts are particularly promising for the development of the methanol synthesis in compact reactors, wherein they can outperform packed-beds thanks to their excellent conductive heat transfer mechanism, independent of the flow velocity [10].

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NOVEL STRUCTURED CATALYTIC SYSTEMS - CARTRIDGES ON THE BASE OF FIBROUS CATALYSTS

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The majority of the oil processing and petrochemical processes are performed under the significant influence of the diffusion limitations. Therefore, the development of the new catalysts with improved mass transfer properties is an important task. The possible promising solution in this area is application of structured catalytic systems using the catalyst on the base of microfibrous supports, produced in the form of cloths, made from glass, mineral, carbon, polymer and other micro-fibers. Such micro-fibrous catalysts (MFCs) may use noble metals (e.g. Pt or Pd) or transient metal (Cu, V, Fe, Ni, etc.) oxides as active components [1-3]. The MFCs may be structured in a form of cartridges with a low pressure drop and with minimized mass transfer limitations, both external and internal. As shown by our theoretical estimation [4], the MFC's cartridges provide the highest unit mass transfer efficiency among all known forms of catalysts, thus highlighting the great engineering potential of structured fiber-glass catalytic systems.

Mass transfer properties of the MFC cartridges were studied experimentally in the reaction of deep oxidation of toluene in air flow using the Pt-containing (~0.07 % Pt mass) commercial glass-fiber catalyst IC-12-S111 (BIC, Russia). Internal mass transfer limitations were eliminated for this catalyst by application of the very thin (<0.4 mm) catalytic fabric, giving the way to separately study the external mass transfer regularities. Experiments included variation of the reaction temperature, air flow rate and the geometry of catalytic cartridges. Pt-based monolith, granulated and wire-mesh catalysts were used as reference catalysts for comparison. The volume of the catalytic cartridge was kept constant in all experiments, though in case of MFC the mass amount of the catalyst in this volume was much lower (less than 150 g per l of the bed) than that for the conventional catalysts.The observed dependence of the apparent reaction rate constant upon flow rate for different types of the catalyst packing is given in Fig. 1. Comparison was made at 350 °C, the reaction rate at such temperature was completely limited by the external mass transfer.

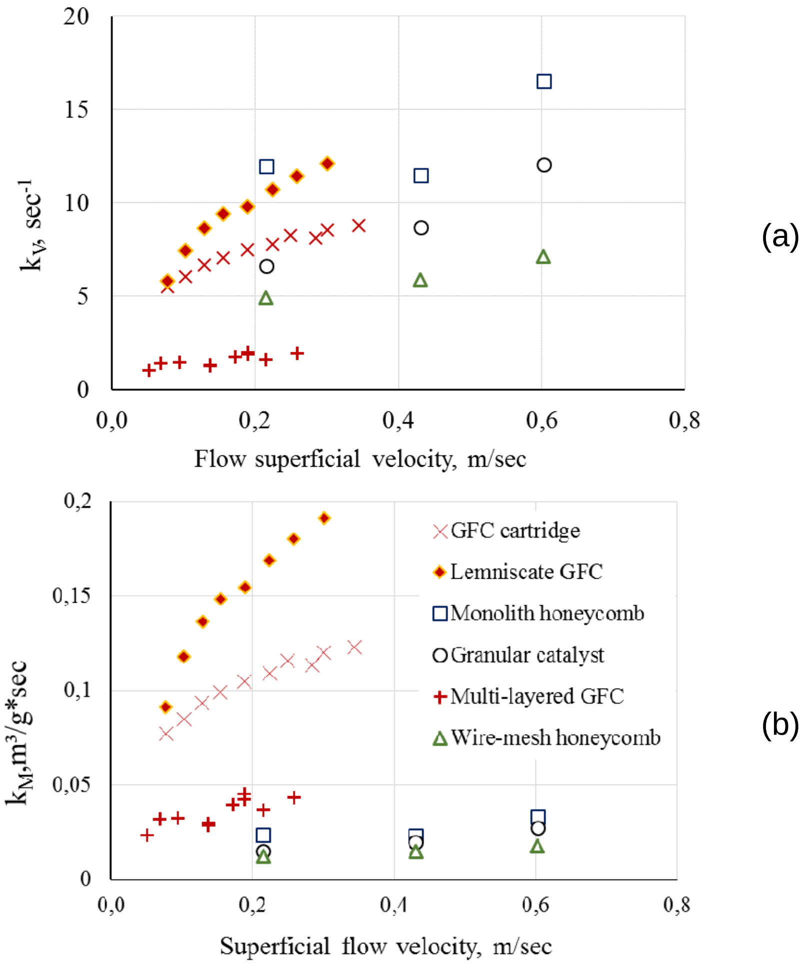

Fig. 1. Dependence of the apparent reaction rate constant upon gas flow rate in the catalyst beds of different structure: (a) – per unit volume of the catalyst bed, (b) – per unit mass of the catalyst

It is seen that the MFC with lemniscate structuring demonstrates the excellent volume performance competitive to that of the monolith catalyst (Fig.1a). At the same time, all MFCs look much more efficient than conventional catalysts in terms of apparent reaction rate per unit catalyst mass (Fig.1b). MFCs may be applied for intensification of various diffusion limited catalytic processes.

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UNDERSTANDING AND CONTROLLING THE INFLUENCES OF MASS TRANSFER ON METAL-ZEOLITE CATALYSTS FOR SELECTIVE OXIDATIONS

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Zeolites are widely used in petrochemical industry for its excellent performance in acid and oxidation catalysis. An additional bonus of zeolites is the shape selectivity, which is endowed by the small sizes of zeolite pores close to molecules. It is very common that a metal is introduced to zeolite to provide additional catalysis function other than acid and oxidation catalysis, such as hydrogenation, dehydrogenation, and reforming, or to provide another different oxidation function.

On metal-zeolite catalyst, the interplay of the different functions determines the overall performance of the catalyst, which involves the transport of reactant and product through the micropores of zeolite and/or intermediate product between sites of different catalytic functions. Additional opportunities are thus available for metal-zeolite catalysts to optimize their performance by manipulating the spatial distribution of metal on zeolite particle to regulate the transport process.

On TS-1 supported gold catalyst used for direct propylene epoxidation in gas phase with oxygen and hydrogen, some carbonaceous deposits such as condensed aromatics and polyalkenes are formed as by products. If the gold nanoparticles are in the micropores of TS-1, these deposits, though in very small amounts, will block the micropores and makes the gold inside the micropores inaccessible. This machnism for catalyst deactivation is validated by tuning the DP process to have different gold nanoparticles inside and outside the micropores[1]. We therefore keep the gold nanoparticles on the external surface of TS-1 by directly using uncalcined TS-1 as support, and consequently greatly improve the stability of the catalyst. Moreover, because the hydroperoxides formed on the corner sites of gold nanoparticles have to migrate to the active Ti^{4+} sites for peroxidation, decreasing the size of gold nanoparticles accelerates the surface migration and therefore increases the hydrogen efficiency.

A second example is the supported Pt catalyst for selective oxidation of hydrogen in presence of propane and propene. This process can be combined with propane dehydrogenation to increase propane conversion and also to provide the heat for dehydrogenation[2]. However, Pt is also very active for propene oxidation. We encapsulate the Pt nanoparticles inside LTA Zeolite (KA) to take the advantage of size exclusion effect. The Pt nanoparticles are accessible only for hydrogen and oxygen. This greatly increases the performance of the catalyst for selective hydrogen oxidation. However, the acid site of the zeolite also catalyzes propene oxidation. In addition, the adsorption of propene on adsorption close to the pore mouth constitutes a big barrier for hydrogen and oxidation to diffuse into the micropores. We therefore neutralize the acidity of zeolite by using alkali, which not only maintains the high activity of catalyst but also increases further the selectivity in hydrogen oxidation.

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ORAL PRESENTATIONS
Section I.
Advances in Chemical Reactor Fundamentals

JOINT KINETICS: A NEW KINETIC STRATEGY FOR HETEROGENEOUS CATALYSIS

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Joint kinetics is presented as a new strategy for chemical kinetics, in particular for heterogeneous catalytic kinetics. Central concepts of joint kinetics proposed in a series of papers [1-11] are “events”, “trends” and “map of events and trends”. “Events” are special features of kinetic dependences observed experimentally or computationally, i.e. extrema and intersections, coincidences and momentary equilibria, “turning points” etc. In analysis of “trends” a special attention is paid to comparing the reciprocal kinetic dependences which start from the symmetrical initial conditions. Maps of kinetic events and trends are constructed and analyzed. Different events are categorized with an indication which events are unavoidable (“always”-events) and which are never happened (“never”-events). Typical models of chemical kinetics are presented:

a) System of differential equations for the batch reactor (astronomic time)
b) System of algebraic equations for the CSTR (space time, or residence time)
c) System of linear equations based on balances of chemical elements and related to the model-free approach.

Within the joint kinetics, the dogma of chemical kinetics “It is impossible to predict kinetic behavior based on known equilibrium thermodynamic characteristics” is corrected. In some cases, knowing the equilibrium thermodynamic characteristics and kinetic dependencies which start from some initial conditions, it is possible to predict kinetic behavior from other initial conditions. This statement is illustrated by examples taken from heterogeneous catalysis (two-step catalytic mechanism, three-step Wei-Prater mechanism of catalytic isomerization and the water-gas shift reaction). A momentary equilibrium in the TAP-studies of reversible adsorption is presented as a source of information about the number of active catalytic centers. The switching point between thermodynamic and kinetic control in organic reactions is analyzed as well.

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A RANKING OF EXPERIMENTS APPROACH FOR THE IDENTIFICATION OF KINETIC MODELS OF ETHYLENE METHOXYCARBONYLATION IN CAPILLARY MICROREACTORS

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Capillary microreactors have proven to be a powerful tool for performing kinetic experiments in multiphase systems, due to the high mass and heat transfer rates they provide, enabling the study of reactions that previously were difficult to be studied in conventional reactors [1-2]. They are more cost effective compared to conventional reactors as the amount of catalyst required is smaller due to the reduced dimensions of the reactor system. Furthermore, flow systems are particularly attractive for kinetic studies as data can be obtained faster and with more precision than in batch systems [3].

Methyl methacrylate (MMA) is an essential building block for acrylic-based products such as resins and adhesives and is used in a wide range of industrial applications. MMA is mainly produced via the acetone cyanhydrin (ACH) route, a route requiring careful management of large quantities of extremely toxic hydrogen cyanide and generating large amounts of acidic ammonium bisulphate waste which has to be recovered by incineration at considerable cost. Conversely, the Alpha Process for the production of MMA is a recent cleaner route based on ethylene methoxycarbonylation involving no by-products and milder operating conditions and requiring around 40 % less production costs compared to the ACH route [4]. The goal of the current work is the investigation of reaction kinetics in the first stage of the Alpha Process, related to the synthesis of methyl propionate (MeP) from ethylene, carbon monoxide and methanol over a homogenous Pd catalyst. The gas-liquid catalytic reaction takes place at moderate temperature and pressures (e.g. typical standard conditions are 100 °C, 10 bara). Experiments were carried out in a flow capillary microreactor, where gas-liquid contact led to a slug-annular flow pattern. Selectivity higher than 99.9 % was achieved.

After a hydrodynamic study to characterise the two-phase flow and mass transfer characteristics, a number of experiments at variable methanol, CO and ethylene concentration in the feed at temperatures in the range 80-120 °C were carried out to screen out the effect of these experimental design factors on the products. A one-dimensional reactor model was developed using the gPROMS platform to describe the observed reaction kinetics. The model included the description of mass transfer and vapour-liquid equilibrium inside the capillary reactor. A ranking of experiments approach, based on model-based experimental design techniques [5], was then used to select the most informative experimental data for the identification of kinetic parameters. These techniques allowed for a precise estimation of kinetic parameters, in such a way that the proposed model was able to describe the experimentally observed system behaviour in an accurate way.

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FIRST-PRINCIPLES ASSESSMENT OF BEP RELATIONS FOR STRUCTURE-DEPENDENT MICROKINETIC MODELING IN HETEROGENEOUS CATALYSIS

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Despite of the fact that the catalyst structure has been an important factor in catalysis science since the discovery of structure sensitive reactions in single crystal studies [1], its effect on reactivity is neglected in state-of-the-art microkinetic modelling. All the details regarding the active site (e.g., prevalent crystallographic planes, edges, corners, defects) are lumped in the concept of an abstract concept of a “free site”, which is uniformly present on the catalyst surface. In reality, the catalyst is dynamic by changing its structure, shape and size in response to the different conditions in the reactor. Thus, the inclusion of such effects within the framework of microkinetic modelling, albeit extremely complex, is of outmost importance in the quest of engineering the chemical transformation at the molecular level [2]. This poses severe challenges for the application of hierarchical approaches, which have been successfully applied for the derivation of structure-less microkinetic models in applied catalysis. Typically, these approaches are based on a first estimation of the kinetic parameters of all the potential elementary reactions at the micro-scale, which is performed by employing computationally non-demanding semi-empirical methods. Therefore, the extension of the hierarchical methodology to the development of structure-dependent microkinetic models requires the derivation and the first-principles assessment of

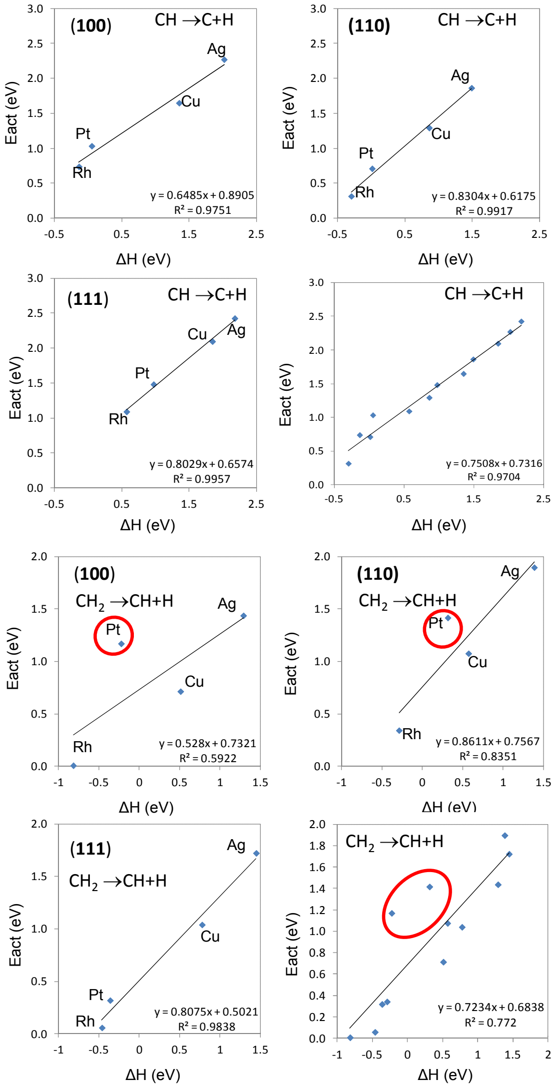

Figure 1. BEP relations for CH dissociation and CH_2 dissociation on different metals and surface structures

semi-empirical relations to predict chemical reactivity at different surfaces. At this scope, in this work, we present a detailed and explicit first-principles assessment of Brønsted-Evans-Polanyi (BEP) relations [3] for the prediction of activation energies of elementary steps at different low-index catalyst surfaces for dissociation reactions on metal catalysts. The analysis has been performed according to a theory-to-theory comparison, following the approach adopted by Maestri and Reuter [4]. We have considered the dissociation reactions of CO, CH and CH_2 on (111), (110) and (100) surfaces of four different metal catalysts (Rh, Pt, Ag and Cu). The activation energy and the structure of the TS have been explicitly calculated for each reaction step on each metal for each surface at two different oxygen coverages (70 reaction pathways in total) by means of periodic plane-wave PBE-DFT calculations (CI-NEB method). We then interpreted the various activation energies, considering different possibilities of correlation (same surface; same metal). Figure 1 reports the different correlations for CH and CH_2 dissociation reactions. We found that BEP relations can correlate quite well the different trends on the different surfaces and metals. Thus, it can be used for the interpretation and prediction of activation energies on different catalyst surfaces. The BEP relation is found to be strongly dependent on the geometry of the TS and by different trends of binding energies for reactants and products among surfaces and metals, which directly concur in establishing the character of the TS. Different interactions/geometries were indeed responsible of a change of the character of TS among the correlating variables, thus negatively affecting the BEP relation. For instance, Figure 1 shows the case of CH_2 dissociation, which presents two outliers in the BEP relations (red circles in Figure 1). Indeed, our calculations reveals that the geometry of the TS changes among the metals and surfaces and in particular the geometry on Pt (110) and Pt (100) surfaces is different with respect to the geometries found on the same surfaces of the other 3 metals. As a result, the character of TS changes, with a direct effect on the slope of the BEP line. On the (111) surfaces, instead, the change in TS geometry is not found by our DFT calculations and consequently the BEP relation holds without any outlier. Extension to edges, corners, defects is currently on going. As a whole, our results show that BEP can correlate the activation energies among the different surfaces and metals for all the considered reactions at reasonable accuracy for the exploration of complex reaction networks towards the development of structure dependent microkinetic models in applied catalysis.

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MINIMIZING DIFFUSION LIMITATIONS IN POROUS CATALYSTS THROUGH RATIONAL DESIGN OF THE MACROPORE NETWORK: APPLICATION TO THE ALKYLATION OF BENZENE WITH ETHYLENE

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Industrial nano/microporous catalysts often operate in the diffusion limited regime, which detrimentally impacts the activity and the selectivity of the catalyst. By introducing a network of large pores with an optimized porosity and an optimized pore size, it is theoretically possible to minimize such transport limitations and increase the utilization of the active catalyst, thereby increasing the volume integrated reaction yield [1]. For zeolite catalysts in particular, recent developments in materials synthesis [2] have clearly shown the importance of introducing mesoporosity around the zeolite phase, in order to provide faster access for reactant and product molecules to and from the active sites. However, the problem of retaining these finely tuned properties from the nanoscale up to the larger length scales of the catalyst pellet or the reactor is often not addressed, and this, in turn, can result in inefficient utilization of the catalyst. Therefore, there is a strong industrial interest in pore network optimization of such hierarchically structured catalysts, and the application of their results to guide the synthesis of more active and selective catalysts.

The vapor phase alkylation of benzene with ethylene over H-ZSM-5 to produce ethylbenzene is an industrially important reaction towards the synthesis of styrene. It is also strongly diffusion controlled, thereby providing a useful case study for the optimization of a broad pore network. To this end, results from quantum chemical calculations, adsorption thermodynamics and diffusion within zeolites [3] are combined in a continuum description of a single catalyst pellet. The pore network is assumed to consist of aggregates of zeolite crystals and mesoporous silica separated by macropores. Diffusion is modeled only through the macropores, with the mesoporous silica acting as a diluent. The diffusion-reaction equation is solved within the pellets, and the volume integrated yield can be calculated as:

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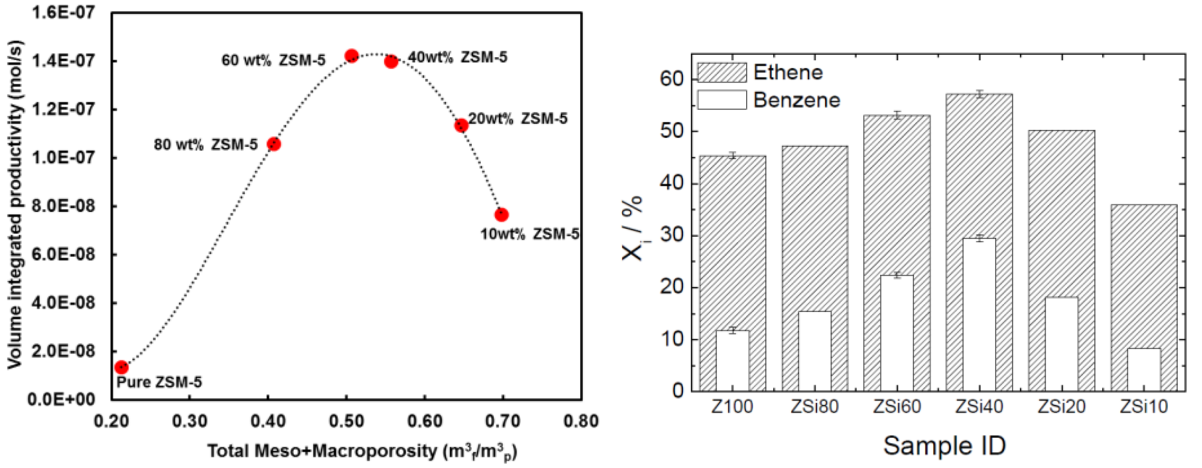
$$\text{Volume integrated yield} = \int_{V_P} \varepsilon_z \rho_z r(p_1, p_2..)\, dV \qquad (1)$$

In equation (1), V_P is the volume of the catalyst pellet, ε_z is the volume fraction of zeolite, ρ_z is the density of the zeolite, r is the rate of reaction and p_i is the partial pressure of species i.



(a) (b)

Figure 1. Results of single pellet simulations (a), and fixed bed reactor experiments (b) of mesopore-ZSM-5 physical mixtures. For the simulations, pellet diameter = 1.6 mm, total pressure = 5 bar, temperature = 653 K. For the reactor experiments, pellet diameter = 280 μm, total pressure = 1 bar, temperature = 623 K

Both simulations of single catalyst pellets, and fixed bed reactor experiments with various zeolite composites show a clear maximum in the yield, indicating a trade-off between better transport to the reaction sites and the volume of catalytic material available for reaction. Furthermore, the qualitative agreement between model and experiments strengthens the case for model driven optimization of the broad pore network to guide the synthesis of highly active catalysts.

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CONVERSION OF DIMETHYL-ETHER TO OLEFINS OVER HZSM-5: REACTION MECHANISM AND KINETICS

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Finding economical alternative routes for light olefin synthesis is one of the main goals for many petrochemical companies. The conversion of natural gas to light olefins is a promising routes in which dimethyl ether (DME), an intermediate that can be synthesized directly from syngas and can be used as a feedstock to produce light olefins (DTO). Selecting a proper catalyst and suitable operating conditions is a key for the implementation of the DTO process.

The synthesis of hydrocarbons from DME is a combination of consecutive reactions where the first reaction helps in converting DME into light olefins. Light olefins may continue to react to form heavy olefins, normal/iso-paraffins, naphthenes and aromatics [1]. Therefore, it is a primary objective during the design of the DTO catalytic process to select the appropriate catalyst that will lead the light olefins to desorb from the active catalyst surface before they are further transformed. In this regard, this work investigated the effect of the SiO_2/Al_2O_3 ratio (30, 80, and 280) on the reactivity properties of the HZSM-5 for light olefins production from DME. The candidate HZSM-5 catalyst with the adequate properties is then employed to investigate the DTO reaction network. This reaction network is based on reactivity runs using neat DME at different temperatures and contact times.

Figure 1 reports DME conversion against time-on-stream (TOS) for ZSM5-280 in the 330-450 °C temperature range. DME conversion and coke formation increased with temperature. However, in the case of ZSM5-280, coke yields were limited to 1.16 wt % with negligible catalyst deactivation. Additionally, ZSM5-280 proved to be selective towards light olefins, particularly propene and butene. For this reason, it has been selected for investigating the DTO reaction network. DTO reaction network is considered based on the carbenium ion chemistry. This was found to best describe the DME surface transformation over HZSM-5 acid sites in which methoxy species plays an important role as a methylating agent. The proposed reaction network considers ethylene and propene as primary intermediates.

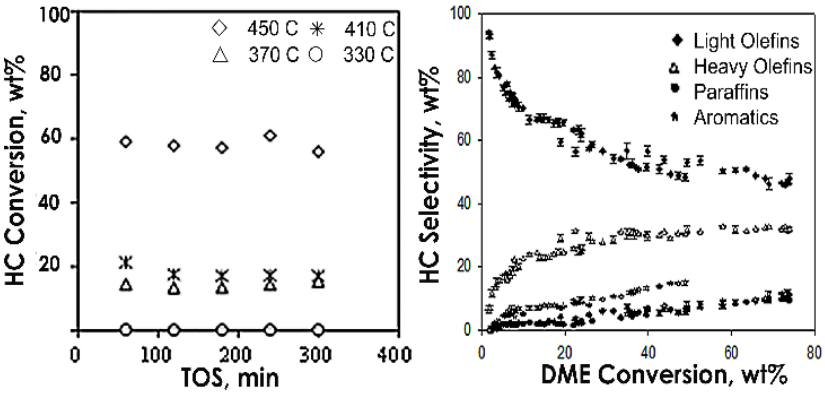

Figure 1. Changes of HC Conversion of DME with time on stream (TOS) at different temperatures and HC selectivity against DME conversion using ZSM5-280 catalysts. Results for ZSM5-30 and ZSM5-80 are reported elsewhere (Al-Dughauther, 2014b)

The formed olefins, then, undergo methylation to their next higher olefins up to octene. In addition, hexene is partially dehydrogenated/condensed forming benzene. Benzene is considered the precursor for the production of heavier aromatics. Benzene is an intermediate species in which its rate of production and transformation are essentially equal. Finally, aromatic species undergo a methyl group addition process. This process becomes slower with the increasing number of methyl groups in the aromatic ring. This proposed model describes a series of 12 sound elementary steps for the DTO reaction network [2]. A kinetic model for DTO was developed using the Langmuir-Hinshelwood approach. This was done with the assumption that all the surface chemical reactions are of first order with respect to the reactants. Each one of the chemical species mole balances with negligible mass transfer limitations across the CSTR like Betty reactor can be written as: $r_i = \frac{F_T y_i - F_{T0} y_{i0}}{W} = \frac{\alpha y_i - y_{i0}}{\tau}$, where, $\alpha = F_T/F_{T0}$, $\tau = W/F_{T0}$, F_{T0} and F_T are the total inlet and outlet molar DME flow rates (mol/hr).

These proposed DTO kinetic model include 12 rate constants and 12 equilibrium constants. Each of these constants has pre-exponential factor and activation energy. Therefore, the total number of parameters to be estimated is 48. It is a challenging task to fit such a large number of parameters with limited number of data points. Therefore, a simplification and reparameterization were done using the experimental data and calculated reaction rates. This simplification resulted in 25 (12 lumped rate pre-exponential factors, 12 activation energies, and one DME adsorption enthalpy) independent parameters to be estimated. Nonetheless, it was a daunting task to estimate statistically significant 25 constants simultaneously. Thus, a step-wise estimation of the kinetic parameters according to the reaction mechanism was completed to minimize the confidence interval and cross-correlation between the parameters. In the first step, regression analysis was performed for the DME reaction rate. This resulted in the estimation of intrinsic kinetic and adsorption constants. This step was followed by the estimation of kinetic parameters for the methylation of light and heavy olefins, hexene aromatization to toluene and aromatics methylation. The results are reported in the following table.

Table 1: Intrinsic Kinetic and Statistical Parameters

Reaction type	k_{0i}*	E_i*	R^2	Reaction type	k_{0i}*	E_i*	R^2
DME dehydration to methoxy species	0.045	184 ± 3	0.96	Hexene methylation to heptane	0.0026	155 ± 7	0.95
DME dehydration to ethylene	0.042	156 ± 6	0.96	Heptene methylation to octane	0.0013	155 ± 7	0.95
Ethylene methylation to propene	0.030	168 ± 3	0.92	Hexene aromatization to toluene	0.1627	84 ± 7	0.94
Propene methylation to butene	0.019	168 ± 3	0.92	Toluene methylation to xylene	0.1808	103 ± 11	0.95
Butene methylation to pentene	0.0081	168 ± 3	0.92	Xylene methylation to mesitylene	0.0012	191 ± 11	0.95
Pentene methylation to hexene	0.0032	155 ± 7	0.95	Mesitylene methylation to durene	0.0005	191 ± 11	0.95

* $k_{0,i}$ in mole $g^{-1}h^{-1}barg^{-1}$ and E_i in $\frac{kJ}{mole}$

With regard to the olefin methylation reactions, one can observe a consistent reduction of the pre-exponential factors from 0.030 to 0.0013. This is expected, given that the measured rate of the olefin methylation is reduced with increasing carbon numbers. A similar outcome is obtained as well for the aromatic methylation reaction in which the calculated pre-exponential factors are reduced from 0.18 to 0.0005. A constant E_i is found for light olefins in the current study, while a steady reduction in the E_i with increasing olefin carbon numbers is reported in the literature. However, E_i is found to increase with the increased methylation of the aromatics, which is in general agreement with the reported literature.

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OP-I-6

MATHEMATICAL MODELLING OF OSCILLATING METHANE OXIDATION IN A CSTR OVER THE WHOLE AND DIVIDED IN HALF Pd FOIL. WHAT'S THE DIFFERENCE?

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The study of kinetic instabilities in man-made and natural reactors showed that a uniform state of interconnected similar cells may be intrinsically unstable and that this instability gives rise to non identical or inhomogeneous stable steady states [1]. In the present study we demonstrate the large difference in the dynamic behavior of methane oxidation over one Pd foil and over two identical pieces of the same foil divided in half and coupled only via the gas phase in a continuous stirred tank reactor (CSTR). The goal of the work is to simulate the experimentally observed unusual anti-phase temperature oscillations of the two identical Pd foils inserted into the same reactor where the reaction of methane oxidation proceeds [2]. The attainment of the dynamic behavior with the anti-phase temperature oscillations of both Pd foils is demonstrated in Fig. 1. It can be seen that the two Pd foils reveal a very different activity before the appearance of the anti-phase temperature oscillations. This striking difference in the dynamic behavior of the two Pd catalysts cannot be explained by the different properties of the two similar foils, because they behave exactly the same way under the other experimental conditions.

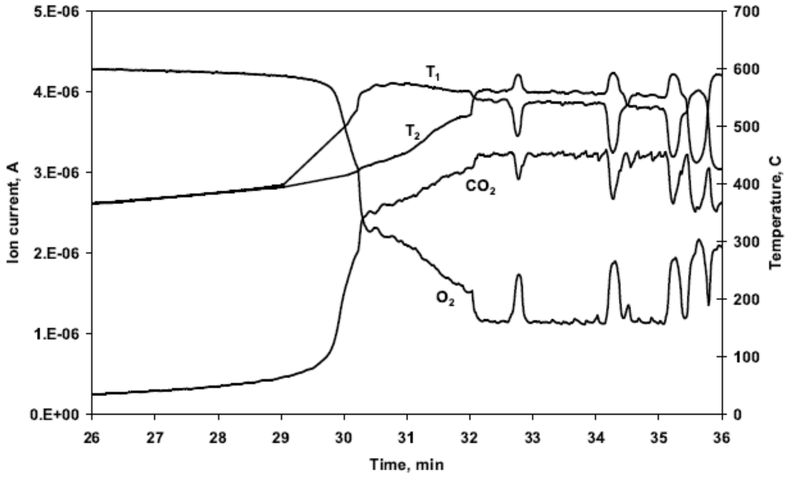

Fig. 1. The attainment of the anti-phase temperature oscillations of two palladium foils at a reactor temperature of 643 K. Reaction mixture: 14.6 % O_2, 81.5 % CH_4 + Ar

Mathematical models, describing the reaction of methane oxidation over one Pd foil and over two identical pieces of the large foil divided in half are presented. At low oxygen pressure the symmetric steady state in the model for the two foils is stable and similar to that in the model of the single foil of a double area. With the inlet oxygen pressure increase the symmetric steady state becomes unstable via the pitch-fork bifurcation, and the two stable asymmetric states emerge. With a further oxygen pressure increase the state of one (active) foil approximately approaches the state of a single foil in the reactor with one foil, while the reaction rate on the other (passive) foil drastically decreases demonstrating that under some conditions only one foil can be active in a reactor with the two identical foils. The symmetry breaking phenomenon is caused by two main factors, namely the limited flow rate of the inlet reactants and the nonisothermal conditions of methane oxidation. In isothermal model the complicated rate oscillations still exist in the considered interval of oxygen partial pressure, but there are no symmetry breaking bifurcations of steady states.

The anti-phase and the in-phase oscillations of the reaction rate on two foils were also obtained in the simulations at low and high oxygen pressure in the agreement with the experimental observations. It was shown that the existence of the anti-phase oscillations is closely connected with the peculiarities of the reaction mechanism of methane oxidation over Pd and the ’unusual’ dependence of the turnover number or the reaction rate per one active center upon the catalyst surface area.

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OP-I-7

OXIDATIVE COUPLING OF METHANE AT ELEVATED PRESSURES: EXPERIMENT AND SIMULATIONS

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The oxidative coupling of methane (OCM) is a promising one-step process for producing ethylene from methane. However, despite all the efforts made, its practical implementation still faces certain difficulties. Among others, the efficiency of the downstream treatment (including separation and chemical processing) of the reaction mixture could be substantially improved in case the OCM reactor is operated at elevated pressure. However, the existing experimental data (see, e.g. [1-5]) demonstrate contradictory effects of elevated pressures onto the efficiency of the target products (C_{2+} hydrocarbons) formation. This study is aimed at the kinetic analysis of effects observed during methane oxidation at elevated pressures in the presence of typical OCM catalysts ($NaWMn/SiO_2$, La/MgO).

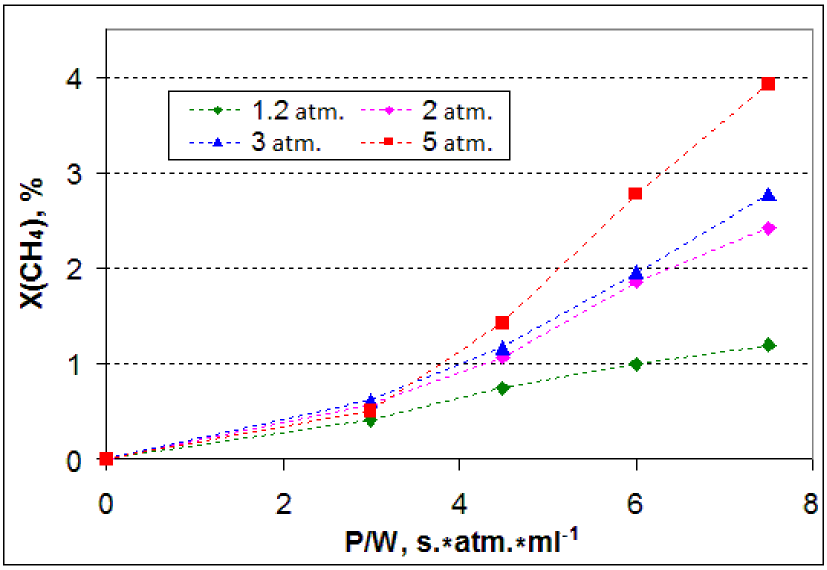

Fig. 1. Methane conversion as a function of (P/W) ratio (see text); 800°C, catalyst - $NaWMn/SiO_2$ (5 mg), $CH_4:O_2 = 91.6 : 8.4$

Experiments were performed in a tubular quartz reactor (i.d. 3.5 mm) with on-line GC-analysis of the reaction mixture in the range of total pressures from 1 to 5 atm. Typical results obtained over $NaWMn/SiO_2$ catalyst are presented on Fig. 1 that shows the effect of the formal residence time (the value proportional to the total pressure in the reactor and reciprocal flow rate measured on the exit of the reactor at atmospheric pressure) onto the conversion of methane. At relatively low residence times the difference between the values of methane conversion at different pressures is nearly negligible, which is consistent with the results of kinetic studies [6], according to which the OCM rate over this catalyst can be described by the redox-type (Mars-van-Krevelen) equation that assumes the apparent reaction order with respect to total pressure of reactants (CH_4 + O_2) close to 1. However, at increasing residence time methane conversion strongly increases with total pressure, likely due to the non-linear development of chain-type reaction in the voids of the reactor, including inter-particle voids in the catalyst layer and in the inert quartz filling.

Testing of several available schemes suggested for modeling of homogeneous methane oxidation demonstrates a large variance of the simulated data on the non-catalytic process (temporal characteristics, product distributions) at typical OCM conditions. Nevertheless, this analysis shows that due to the strong effect of pressure onto the overall rate and selectivity to C_{2+} hydrocarbons, the higher the pressure, the more intense the formation of side products of methane oxidation (oxygenates, carbon oxides) in the voids of the reactor.

Taking into account complex effects of kinetic conjugation observed both in homogeneous oxidation and in the presence of OCM catalysts and "inert" materials (such as quartz) [7], one may conclude that the overall behavior of the system (reactor + internals + catalyst) at elevated pressures can be analyzed and optimized in the framework of advanced description that accounts the differences in reaction kinetics in different zones.

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OP-I-8

COMPARATIVE STUDY OF MTO KINETICS OVER SAPO-34 CATALYST IN FIXED AND FLUIDIZED BED REACTORS

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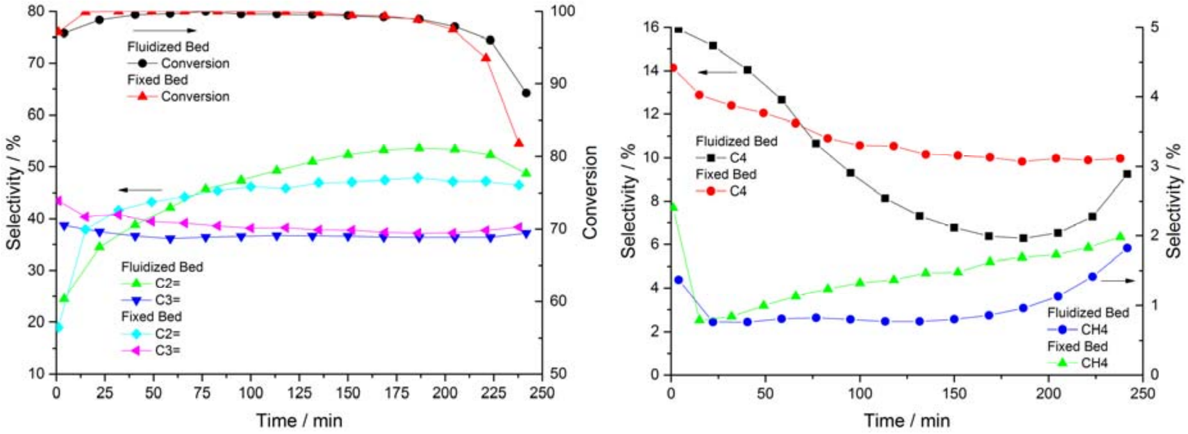
The methanol to olefins (MTO) process has been received consierable interests due to its importance in transforming aboundant researves such as coal, natural gas and biomass to widely demanded light olefins. Two types of zeolite catalyst, i.e. the SAPO-34 and ZSM-5, are found more efficient in MTO process compared to other catalysts. Recently the MTO process based on SAPO-34 catalyst has been sucessfully commercialized in China, in which the fluidized bed reactor-regenerator system was used because of the rapid deactivation of SAPO-34 catalyst. The kinetics of MTO process over SAPO-34 catalyst is therefore of great significance in designing and optimizing the industrtail MTO reactors. The kinetics has been extensively studied via experiments in either fixed or fluidized bed reactors, however, notable variations in product selectivities are observed in these two types of reactors. In this work, a comparative study on MTO kinetics in fixed and fluidized bed reactors will be conducted. We first analyze the difference and discuss the underlying mechanisms leading to the difference. Based on the analysis we try to establish an modelling approach to unite the kinetics obtained from fixed bed reactor and fluidized bed reactor.

Figure 1 shows the conversion of methanol and selectvities to CH_4, C_2H_4, C_3H_6, and C_4 in the product in both micro-scale fixed bed and fluidized bed reactors under the same operation conditions. As can be seen, the selectivities to CH_4, C_2H_4, and C_4 show quite different trends with time on stream (TOS), whileas the conversion of methanol and selectivity to propylene demonstrate similar behavior, which could be attributed to catalyst shape selectivity due to coke deposition.[1] The difference is explained by the inhomogeneous distributed coke deposition in fixed bed reactor. The catalyst bed in a fixed bed reactor could be divided into three zones: initiation, autocatalytic and product zone.[2] Only part of the catalyst participates in the direct conversion of methanol in fixed bed. This fraction of catalyst accumulates coke much faster than the corresponding fluidized bed reactor. When this fraction of catalyst deactivates, the next fraction of catalyst takes its role, thus forming a moving coke front[3].



(a) (b)

Fig. 1. Product selectivities of MTO process in fixed bed reactor and fluidized bed reactor as a function of time on stream. (a) Conversion of methanol, and the selectvities to ethylene and propylene; (b) the selectivities to C_4 and CH_4

Note that in fluidized bed reactor the mixing of catalyst is very fast, the distribution of coke deposition can be considered uniform. In this way, a modelling approach is established to describe the evolution of coke distribution in fixed bed reactor in terms of the coking rate. If the coking rate is assumed as the same as that in the fluidized bed reactor, we can unite the kinetics of methanol conversion over SAPO-34 catalyst in both fixed bed and fluidized bed reactor.

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OP-I-9

CONTINUOUS FLOW PACKED BED MICROREACTORS USED FOR DEACTIVATION STUDIES OF AEROBIC ALCOHOL OXIDATION ON Au-Pd/TiO_2 CATALYST

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Selective oxidation of alcohols is an important reaction in organic chemistry and often performed with stoichiometric inorganic reagents.[1] In recent years, there has been a growing demand for the development of heterogeneous catalysts for oxidation of alcohols with molecular oxygen, since it is a green and efficient process.[2-3] However, large-scale applications of aerobic alcohol oxidation are still limited to few catalysts with sufficient reactivity and stability.[4]

Herein, the stability of a bimetallic Au-Pd/TiO_2 catalyst was examined in a packed bed microreactor for the oxidation of cinnamyl alcohol dissolved in toluene. The catalyst was prepared by co-impregnation with a Au-Pd weight ratio of 1:19 [5]. Experiments were performed at 80-120 °C, oxygen concentration 0-100 % and total pressure 4 bara. Principal products observed were cinnamaldehyde, 3-phenyl-1-propanol and *trans*-β-methylstyrene. Although the same catalyst was shown to possess good stability in the oxidation of benzyl alcohol, it deactivated during the oxidation of cinnamyl alcohol particularly at elevated reaction temperatures.

Higher concentration of oxygen used for the reaction led to an increased cinnamaldehyde selectivity but lower conversion and higher deactivation rates. Treatment with hydrogen recovered only a fraction of activity. Pd was detected in the reactor effluent during cinnamyl alcohol oxidation. Thus, Pd leaching and the presence of oxygen seem to be causes for catalyst deactivation. The higher deactivation rates and amount of Pd leached at higher oxygen concentration, along with partial recovery of activity after hydrogen treatment, indicate that the role of oxygen is complex, affecting deactivation in various ways (possibly including competing with alcohol on the catalyst, removing by-products from surface, accelerating Pd leaching). Switching substrates between benzyl alcohol and cinnamyl alcohol showed deactivation during cinnamyl alcohol oxidation but steady performance during benzyl alcohol oxidation, demonstrating different deactivation characteristics for the two reactions.

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OP-I-10

CONTINUOUS NANOSTRUCTURED METAL OXIDES AND METAL PARTICLES MANUFACTURING BY MICROWAVE IRRADIATED FLOW SYSTEM

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Developing energy efficient, reproducible and high throughput synthetic approaches to nanomaterials manufacturing has gained increasing attention over the past decades due to their multifunctional properties. Herein crystalline nanostructured metal and metal oxide have been engineered by a novel microwave powered flow system.

We first prepared ellipsoid hematite superstructures (Hem-SS) in ~6 min residence time without employing any surfactants or templates using $Fe(NO_3)_3{\cdot}9H_2O$ as the only precursor in aqueous solution at atmospheric pressure. Microwave irradiation was found to direct the self-assembly of produced hematite subunits via selective heating and polarization of nanoparticles. Concentration and flow rate of the precursor solution were also found to be critical to Hem-SS synthesis. Little crystalline hematite particles were observed at high precursor concentrations (0.1 and 0.2 mol L-1). No hematite particle formation was observed at higher flow rates, indicating the significance of the amount of microwave energy absorbed per unit time.[1] However conventional heating was not able to produce pure hematite under identical conditions (e.g. at 120 °C.) and even at higher temperature of 140 °C. In parallel, the novel technology can manufacture Au nanoparticles with mean particle of ~4 nm x ~8 nm after 90 s microwave irradiation (Fig. 1).[2] The developed sustainable process that benefits from both microwave chemistry and flow technology is reproducible and has the potential to fabricate other metal/metal oxide nanoparticles or their self-assembled superstructures. All these results will be presented in the conference.

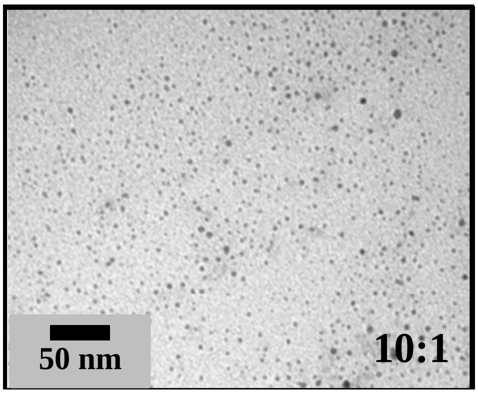

Fig. 1. TEM images of the Au-NPs synthesized under microwave power of 36 W, 4 mL min^{-1} flow rate and citrate-to-gold precursor molar ratios of 1 to 10

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OP-I-11

HIERARCHICAL ANALYSIS OF THE GAS-TO-PARTICLE HEAT AND MASS TRANSFER IN MICRO PACKED BED REACTORS

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Fundamental multi-scale modeling of chemical reactors is considered as one of the most promising frontiers for chemical reaction engineering and is becoming a very powerful tool for the analysis and design of novel catalytic reactors [1]. This approach is based on the multiscale simulation of the reactor behavior by means of parameters and descriptors, which are directly linked to theoretical accessible phenomena. This approach, however, is intrinsically limited by the required computational time, which can be very demanding even for simple cases. As a result, routinely reactor analysis and design have still to resort to simplified and lumped models, which rely on phenomenological descriptions based on an empirical understanding of the involved phenomena [2]. As such, their validity is often limited to the experimental conditions considered for the derivation.

A promising and convenient solution to this problem is represented by the application of hierarchical approaches [3]. In essence, detailed and computationally demanding analyses – based on computational fluid dynamics simulations (CFD) of the reactor – are first used to study in detail a selected and limited number of conditions. Then, the CFD results are interpreted by means of 1D heterogeneous models for the derivation of lumped parameters to be used in classical reactor models. On one side, this approach limits the use of computationally demanding simulations. On the other side, it allows for the rational derivation of parameters, which are related to a detailed and sound description of the governing phenomena. This approach can be particularly useful in the analysis and design of novel micro-reactor configurations, where the classical correlations for the evaluation of transport coefficients are not yet established and validated. In this respect, the hierarchical analysis by means of CFD simulations can allow for a sound analysis and assessment of the parameters, which have been derived at different operating conditions and reactor configurations. For instance, this is the case of micro packed bed reactors [3], which have been proposed as a promising alternative to the multi-tubular fixed bed reactor for highly exothermic reactions [4]. At this scope, three different micro packed beds with different values of tube-to-particle diameter ratio are generated and their transport properties in terms of mass and heat transfer coefficients are analyzed by means of CFD and 1D models. First, we performed a detailed CFD analysis of heat and mass transport on different geometries of micro-packed beds. Such an analysis has been then interpreted by means of 1D heterogeneous models of the reactor in order to develop suitable correlations for the gas-to-particle heat and mass transfer properties in micro packed bed reactors. Figure 1 shows that there is no substantial difference between the j-factors for heat and mass transfer in agreement with the Chilton-Colburn analogy. Also, on the basis of the CFD simulations, we derived a suitable correlation, which predicts the variation of j-factor as a function of the flow conditions (Figure 1).

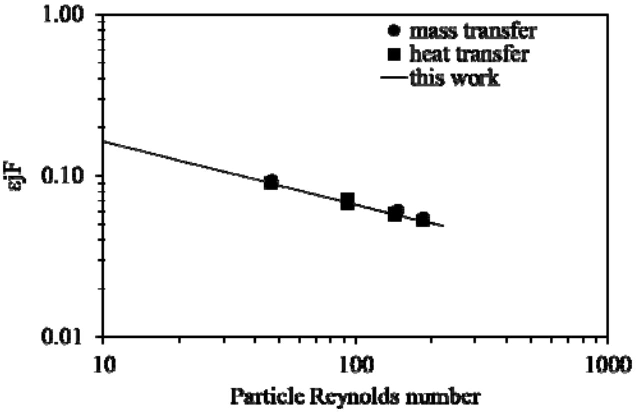

Figure 1. Chilton-Colburn analogy for micro packed beds

The prediction of the 1D heterogeneous model incorporating such hierarchically derived correlation was found to be in excellent agreement with the CFD simulations, as shown in Figure 2. Therefore, this indicates that the CFD-based correlation for transport properties fully retains all the main features of the detailed CFD simulation. Thus, on a more general basis, this work clearly demonstrates the potentiality of the hierarchical derivation of transport parameters in reactor engineering, which can be employed for the efficient and fundamental analysis and design of novel reactor technologies.

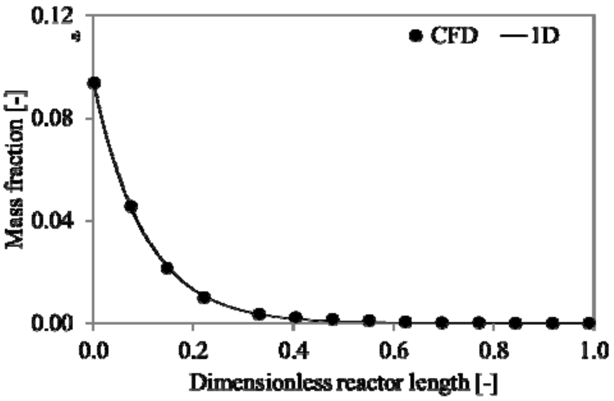

Figure 2. Comparison between the CFD and 1D heterogeneous model

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OP-I-12

CATALYTIC BENZYL ALCOHOL OXIDATION IN A THREE PHASE MICRO-PACKED BED REACTOR: HYDRODYNAMICS, MASS TRANSFER AND DEACTIVATION

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The performance of a three-phase flow packed-bed reactor can be significantly affected by factors such as hydrodynamics, mass transfer and particle size. The hydrodynamics can have an even further complex influence, in that it can affect the mode of deactivation of the catalyst. Microreactors are commonly known for their high heat and mass transfer rates. However, they have high liquid hold-up as a result of the high capillary forces in comparison to conventional trickle bed reactors, leading to significant liquid phase mass transfer resistances in the radial direction [1]. Benzyl alcohol oxidation on TiO_2 supported Au-Pd catalyst has two main reaction pathways: one that relies on oxygen, producing the desired product (benzaldehyde), whilst another anaerobic pathway produces the by-product toluene [2]. Thus, the liquid phase resistance to mass transfer in such a reaction can have serious implications on product selectivity. This study assesses the interaction between hydrodynamics, mass transfer and deactivation on Au-Pd catalysed benzyl alcohol oxidation.

A microfluidic experimental setup was used to deliver liquid alcohol and oxygen gas to a serpentine channel reactor (**Figure 1**) with a 300 μm x 600 μm cross-sectional area. The temperature was controlled at 120 °C and the pressure regulated to 1 barg. The catalyst used was highly active Au-Pd/TiO_2 with an average particle size of 65 μm.

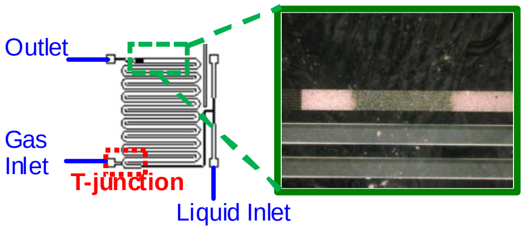

Figure 1. Schematic of micro-packed bed

The hydrodynamics and particle size had profound influences on the mass transfer characteristics in the micro-packed bed reactor. **Figure 2** indicates the presence of both external and internal mass transfer resistances. Operating in the gas-continuous regime (a flow regime characterized by a liquid film covering the

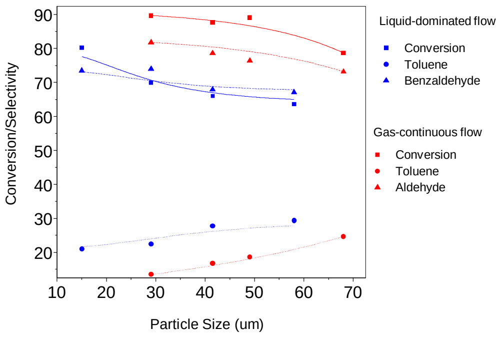

Figure 2. Effect of particle size and flow regime on reaction performance

particle surface with a gas-continuous flow path) led to enhanced external mass transfer. This caused a shift in the dominating reaction pathway, resulting in higher benzaldehyde selectivity and benzyl alcohol conversion. The catalyst particles used here represent a 100-fold increase in the surface-to-volume ratio in comparison to conventional laboratory reactors. Despite the small diameter particles used, internal mass transfer limitations exist due to the high catalytic activity, as evidenced by increasing conversion with decreasing particle size. Hydrodynamics also had implications on the stability of the catalyst – possibly linked to the tendency of high boiling point by-products such as benzyl benzoate and dibenzyl ether to deposit on the catalyst surface. This was particularly prevalent at high Gas:Liquid (G:L) ratios, where in the absence of gas-liquid slugs, heavy compounds likely deposited and accumulated in the catalyst pores, causing hysteresis behavior in the activity with decreasing gas flowrate (**Figure 3**). Catalyst dilution with TiO_2 support particles of the same size was used to characterize mass transfer in the liquid-dominated flow regime (a flow regime characterized by large liquid slugs occupying the majority of the bed and covering the particle interstitial voids, while the gas forms large elongated slugs). By plotting the inverse of reaction rate vs. inverse of catalyst content, the gas liquid mass transfer coefficient was found to be 23.6 s^{-1} (**Figure 4**). This is much higher than that commonly observed in conventional trickle bed reactors.

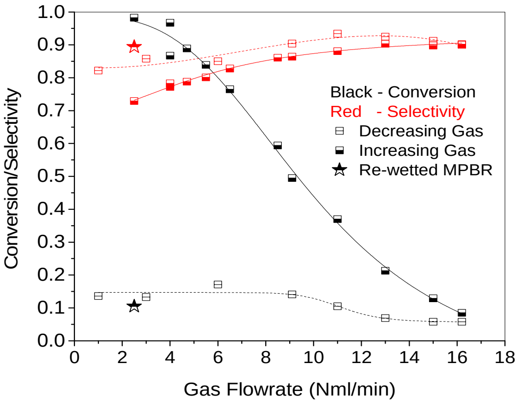

Figure 3. Hysteresis behaviour with changing in gas flowrate

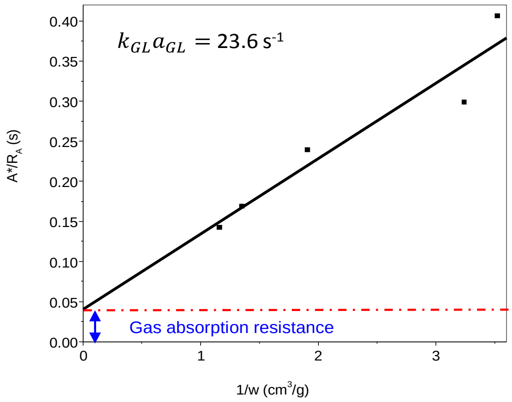

Figure 4. Packed bed reactor mass transfer characterization

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HYDRODYNAMICS AND MASS TRANSFER IN A TRICKLE BED REACTOR WITH FOAM PACKING

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Trickle-beds with random particles, such as spheres, Raschig rings, etc., are widely used in industry for gas-liquid reactions. Structured packings, such as monoliths, are also used commonly, mainly because of their lower pressure drop. On the other hand, monoliths present drawbacks, e.g. relatively thick walls, fragility, and low thermal conductivity for ceramic monoliths, high cost for metallic monoliths, and for both, limited mass transfer due to the laminar flow in their channels.

Foams are a new type of structured parking that allows operation with enhanced mass and heat transfer with low pressure drop, due to their high porosity, surface area and tortuosity. Foams have been proposed as supports for heterogeneous catalysts for fixed bed and trickle bed reactors, but their properties make them potentially adequate also for mass transfer limited gas-liquid reactions.

The scope of this work is to study the hydrodynamics and mass transfer in trickled beds with foam packings. For this purpose, residence time and mass transfer have been characterized. These properties are very important in order to assess the efficiency of foams for gas-liquid reactions.

Two commercial foams have been studied: an alumina based, with 20 ppi and porosity 0.88 (foam 1), and a SIC based, with 7 ppi and porosity 0.80 (foam 2). Foam blocks of 45 mm diameter and 190 mm total length were placed in a flanged stainless steel tube. The bed was operated in co-current down-flow, with continuous liquid (water) and gaseous feed (air) in trickle regime, at ambient conditions.

Liquid residence time distributions have been measured by tracer experiments [1], injecting pulses of aqueous NaCl and measuring the conductivity at the bed exit. Results, corrected with blank experiments, were modelled according to the axial dispersion model, and Bodenstein numbers, $Bo = (u_L\ d_t)/\ D_{ax}$ (were d_t is the pore cell size) were calculated. Bo was found to decrease with Reynolds numbers, $Re = (\rho\ u\ d_t)/\ \mu$, both in the liquid and gas, and to be greater for foam 1.

Liquid holdup was also calculated from residence time distribution data. Dynamic holdup increases markedly with liquid superficial velocity, while the influence of gas superficial velocity is less marked. Dynamic hold up was correlated with Re in gas and liquid phases using equations similar to the used for the Bodenstein number.

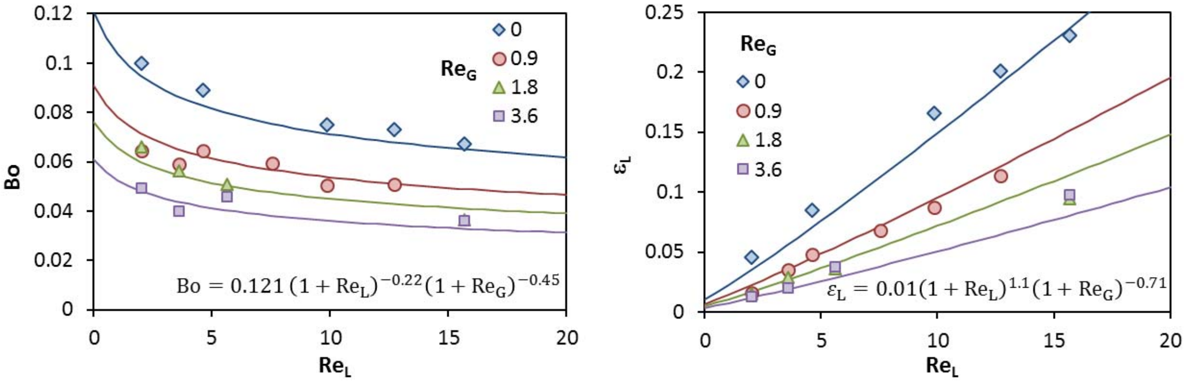

Fig. 1. Axial dispersion (Bo) and liquid hold-up (ε_L) for foam 2, as a function of Re in the gas and liquid. Symbols correspond to experimental results and lines to model fittings

Gas to liquid mass transfer has been studied by reaction of carbon dioxide from the gas phase with aqueous sodium hydroxide, analysing the carbonates formed. Experimental results allow calculating the gas-liquid mass transfer coefficient and interfacial effective area, as detailed in [2].

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DESIGN OF A MILLIFLUIDIC HIGH PRESSURE, HIGH TEMPERATURE TRANSPARENT REACTOR FOR SPECTROSCOPIC REACTION FOLLOW-UP

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Context and objectives

Hydrodesulfurization (HDS) catalysts are experiencing a faster evolution than ever. In order to speed up the knowledge acquisition, it is of interest to acquire data about what is occurring inside the reactor in real time. Some of the analytical techniques [1] developed for effluent and catalyst phases characterization like Raman spectroscopy can be used in HDS conditions.

In this paper, we present the design of a high pressure, high temperature transparent reactor, suitable for Raman spectroscopy investigation as well as the development of a Raman-based characterization method to acquire real-time spectra in various spots along the reactor during diesel HDS.

Set-up principle

The chosen reactor is a cylindrical quartz tube with inner diameter slightly larger than the pellets diameter tightly enclosed in a Joule effect heated stainless steel tube with a slit window for optical access (Figure 1). To acquire spectra along the reactor without being invasive, we opted to use a long working distance objective and to place the set-up on a x-y-z moving stage.

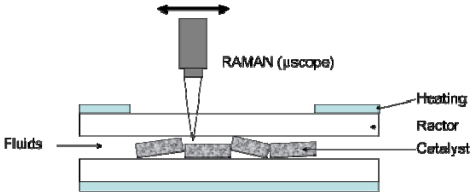

Figure 1. Principle of the set-up

Technical and analytical challenges

Reactor has to withstand operation at 30 bar and 350 °C and provide an isothermal length of 10 cm. Additional constraints are 1) a weight less than 1 kg (maximum for the microscope moving stage) and 2) the objective lens should not be more than 1 cm away from the catalyst surface.

The first Raman spectra acquisition challenge, before optimization of the analytical parameters, is to adjust perfectly the focusing of the laser beam on the randomly positioned pellets surface.

Solutions

The stainless steel tube heater geometry was optimized (using Comsol Multiphysics).

The optimized design proved to ensure a 10 cm isothermal profile along the reactor length with a good agreement between experimental and simulated values (Figure 2).

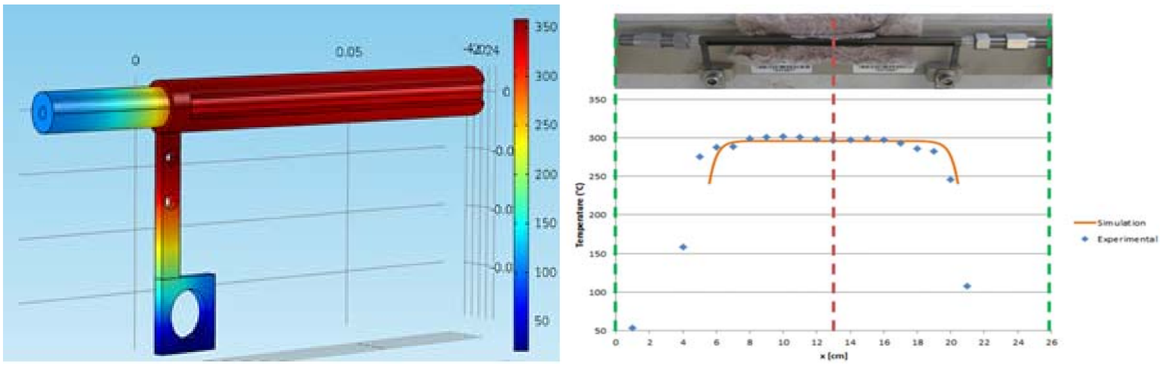

Figure 2. Temperature profiles. Left : 3D view of half of the geometry; Right: simulated (curve) and experimental (points) temperature profiles along the reactor length

We discovered that optical reflection on the system presented very different patterns depending on the focusing height and that when the focus point is on the solid, the image present a wide line parallel to tube axis. Using that characteristics, we are able to determine where to focus without any laser exposure, thus reducing the risk of sample over-heating.

By performing Raman analysis (at the focus point), over the surface of a catalyst particle within the quartz reactor full of diesel, we observe that the presence of diesel only impacts the lower wavelength of the spectra, so that the most interesting catalysts bands located on the other side are still resolved. (Figure 3).

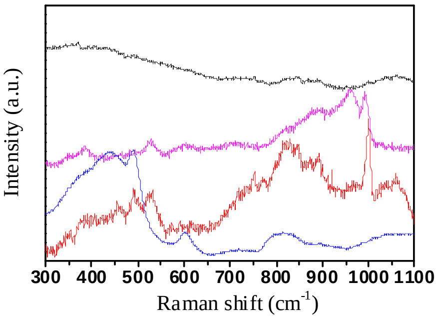

Figure 3. Spectrums of quartz (blue), diesel (black), catalyst (pink) and of the catalyst inside a quartz reactor full of diesel (red)

Conclusions and perspectives

A design of reactor has been achieved to perform HDS of GO in a transparent reactor at 350 °C, 30 bar with an isothermal profiles. It was possible to perform Raman analysis on the catalyst surface, when the particles are randomly placed inside the reactor full of diesel at room temperature.

Next steps concern the validation of the reactor in HDS conditions and acquire spectra with liquid flow, gas flow, and ultimately during catalysts activation and HDS reaction.

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ON THE HYDRODYNAMICS OF MEMBRANE ASSISTED FLUIDIZED BED REACTORS USING 3D X-RAY ANALYSIS

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Introduction

Recently fluidized bed membrane reactors have been extensively studied for equilibrium limited reactions due to their high degree of process intensification achieved by integrating perm selective membranes in the reactor combined with excellent mass and heat transfer characteristics of fluidization. The hydrodynamics in these reactors can be significantly affected by the presence and permeation through high flux membranes, affecting the bubble phase properties (enhanced bubble break-up) and the solids hold up distribution and circulation patterns close by the membranes (formation of densified zones). Experimental observations on the effects of internals [1] or flat membranes integrated in the side walls [2] on the performance of pseudo-2D bubbling fluidized beds have been reported in the literature, but no study has yet been performed on a real 3D membrane reactor. This research aims to extend fundamental understanding on the hydrodynamics of bubbling fluidized bed reactors with highly permeable immersed vertical membranes for gas extraction.

Experimental

The hydrodynamics of a 3D membrane reactor geometry for small scale applications (i.d.: 100 mm) (see Figure 1) has been investigated using a 3D X-ray tomography setup described elsewhere [1]. Three detector plates

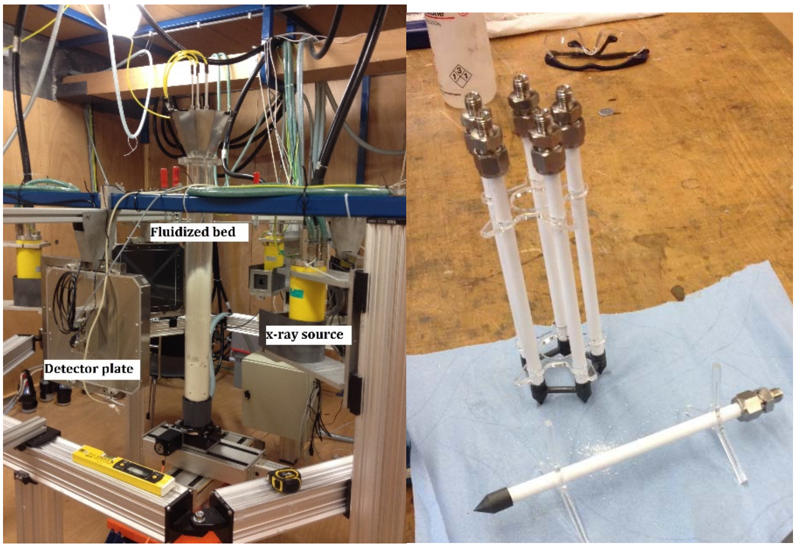

Figure 1. Picture of the fluidized bed membrane reactor in the center of the setup and membrane modules

(30x30 cm) with a resolution of 0.2 mm per pixel were used to measure the output X-ray signal through the reactor.

Initially the fluidization behavior of the reactor was investigated using Geldart B (ca. 500 μm polystyrene) and A/B type particles (80-200 μm alumina) in absence of the membrane module, quantifying the time averaged bubble hold-up, bubble size distribution and bubble rise velocity for different inlet flow rates and particle types. The possibility of slug formation at various fluidization velocities was investigated and recommendations for the membrane reactor design and operation are given accordingly. In the second step, different numbers of ceramic porous membranes (alumina 100 nm pore size at the surface) of 200 mm in length and 10 mm outer diameter were submerged inside the fluidized bed down to the distributor plate (a porous stainless steel with 40 μm pore size). The change in bubble phase properties and bed fluidization behavior was studied, first without gas extraction via the membrane tubes and subsequently with gas extraction with different gas extraction flow rates (up to 40 ln/min). The solids hold up near by the membranes were monitored for a small region of interest with high resolution (0.2 mm). The possibility of the formation of densified zones is discussed and their nature (dynamic/static) is characterized in time and length scales.

Results

As an example, Figure 2 and 3 show typical output intensity profiles for a projected pixel line of a cross section of the reactor with one immersed membrane in the middle of the reactor without gas extraction (selected snapshots from 1 minute of data acquisition and with 35 frames per second).

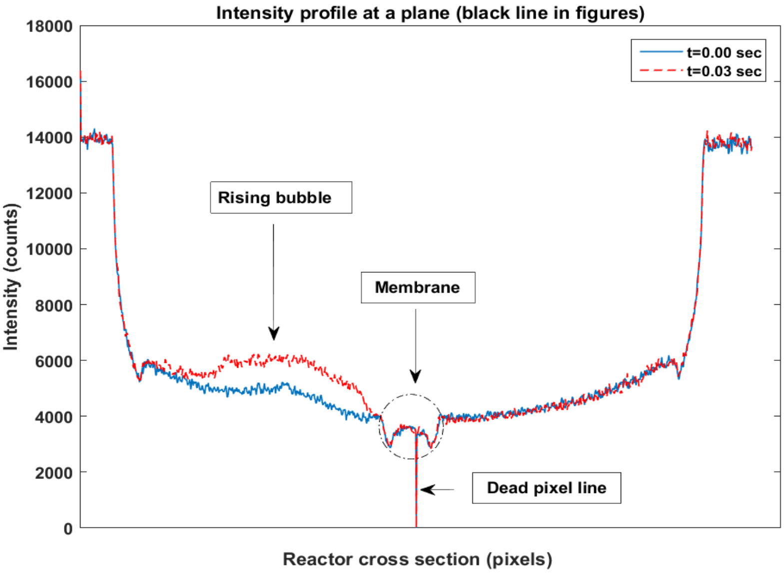

Figure 2. Output intensity profile at a specific reactor plane

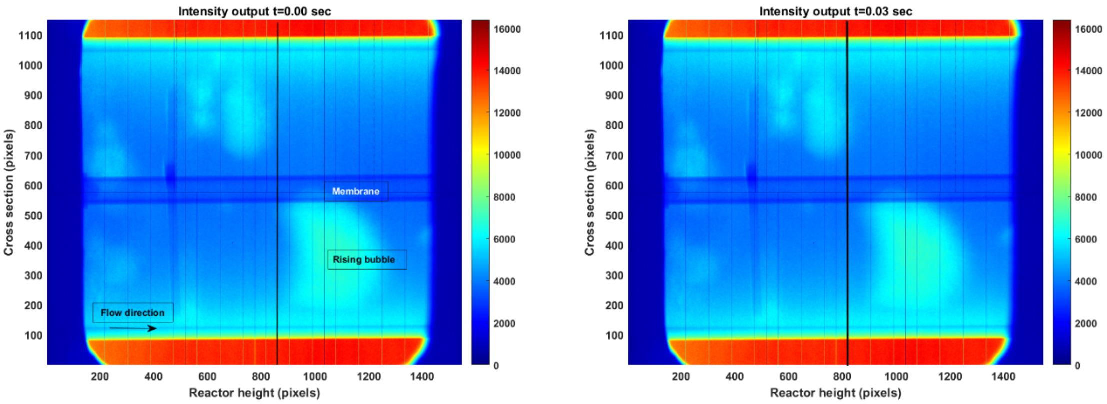

Figure 3. Output intensity map (Note that the picture has been rotated 90°)

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OP-I-16

INVESTIGATION OF BEHAVIORS OF THE CIRCULATING FLUIDIZED BED

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Catalytic processes using a circulating fluidized bed of solid catalyst particles of type B by Geldart classification widely used in the chemical and petroleum industries. To ensure a uniform structure of fluidized bed gas-solid distributors were installed in a reactor frequently.

In the present study it was investigated the effect of the gas-solid distributor on a hydrodynamic modes of the circulating fluidized bed. The distributor in the shape of four rows of baffles commonly referred to as "sheds" with 90° included-top angle was used.

The study was carried out with the CFD method. The Eulerian−Eulerian approach was used for the simulations of hydrodynamics of gas−solid flow. Comparisons were performed with experimental results obtained in the cold model of circulating fluidized bed with 0.7 m diameter. The industrial fluid bed Cr_2O_3/Al_2O_3 catalyst "KDM-M" was used in experimental set-up. The pressure from fluidized bed was measured and a time-series, frequency and state-space analysis of pressure data was used.

PATTERNING FLUIDIZED BED DYNAMICS VIA PULSED FLOW

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Fluidized bed reactors are broadly used in industrial applications that require a good contact between a solid and a gas phase, such as gasification, combustion, or fluid catalytic craking. The non-linear nature of the gas-particle and particle-particle interaction combined with the collective behavior of granular matter generates meso and macro-scale dynamics that are tremendously complex, complicating the design, control, and scale-up of fluidized bed reactors [1].

A way to address these challenges is imposing more regular dynamics in the reactor, something that can be achieved by using the pattern forming capabilities of granular matter when excited with an oscillating force [2]. This concept has been shown experimentally in beds fluidized with an oscillating gas flow, which can adopt a variety of regular configurations [3, 4] (Fig. 1). In quasi-2D geometry, bubbles form near the distributor in fixed, alternating positions, generating a hexagonal bubble pattern when they rise through the bed. In shallow 3D beds, the pattern manifests itself as stripes and squares on the bed surface.

This collective behavior has interesting potential applications in fluidized bed reactor engineering. On the one hand, it is an excellent way to control the bubble size in the reactor and minimize gas bypassing. On the other hand, the wavelength of the patterns is independent of bed diameter, which is promising from the point of view of scaling-up. The fundamental physics behind this striking phenomenon can also be used to test computational fluid-dynamics models as a function of their pattern forming capabilities [5].

In this contribution, we discuss our latest experimental and computational insights about pattern formation in fluidized beds and how these patterns can help us to understand and engineer fluidized bed reactors.

OP-I-17

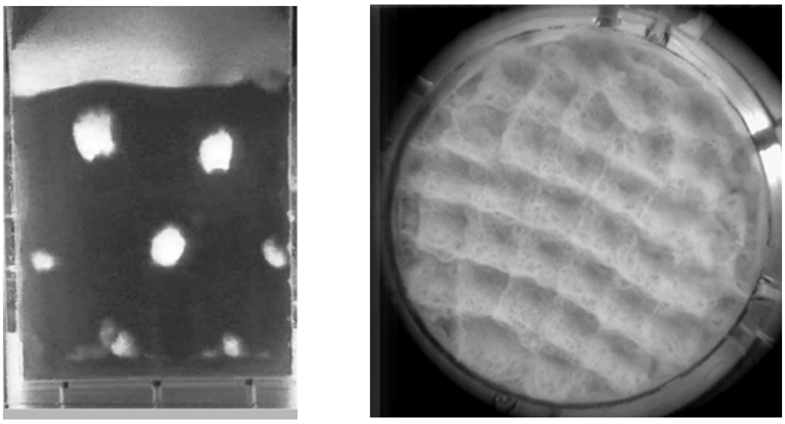

Fig. 1. Pattern formation in a quasi-2D bed (left) and a shallow 3D bed (right)

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Acknowledgements

The research leading to these results has received funding from an EPSRC Frontier Engineering Award (EP/K038656/1).

IMPACT OF FEED TEMPERATURE RAMP ON DYNAMIC AND STEADY STATE MULTIPLICITY IN A MONOLITH

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Kinetic parameters and ignition temperatures in monolith reactors are often determined by measuring the effluent conversion (or temperature) following a constant rate feed temperature ramp up (usually past the light-off value) followed by a ramp down. Experiments reveal that the light-off curves, describing the effluent conversion as a function of the feed temperature, following a ramp up often differ from those following a ramp down. This behavior is referred to as *dynamic hysteresis*. The temperature in a reactor is affected by the axial and transversal heat conduction in the reactor. Thus, during a feed temperature ramp there is a delay in the response of the solid temperature to the change in the feed temperature. Specifically, under a fast ramp up (down) rate, the temperature at the monolith downstream (upstream) is lower (higher) than under a steady state with same feed temperature. Hence, the ramp shifts the dynamic ignition temperature to higher values and the extinction temperature to lower values. If this shift is not properly accounted for, it will lead to erroneous predictions of the reaction kinetic parameters and the ignition temperature. A dynamic hysteresis may occur even under ideal conditions (e.g. plug flow and negligible heat generation by the reaction) and is fundamentally different from the steady-state hysteresis, which is generated by the heat released by the reaction and the thermal feedback. Experimentally or in simulation studies, a thermal multiplicity hysteresis may be attained by a very slow ramping rate.

We present predictions for the width of the dynamic hysteresis loop for a case with negligible heat effects ($\Delta T_{ad} = 0$) using two limiting reactor models: a pseudo-homogeneous and a two phase plug flow model. These predictions point out the impact of the feed temperature ramp rate, the heat capacity ratio between the solid catalyst and the gaseous reactant, the space time and the heat Peclet number. When the heat effects are not negligible, the light up is affected by both the thermal and dynamic hysteresis.

In many emission reduction processes, one needs to combust all the pollutants in the effluent. When the various individual reactants ignite in a narrow temperature range, they all ignite in that range. A current open question is if the effluent contains species with rather different ignition temperatures what adjustment in the feed composition and ramp rate can ignite all the species at essentially the same temperature (simultaneous ignition). A general analysis for the n-species case of is beyond the scope of this study.

We report an analysis of the two reactants case, using as an example the co-oxidation of a CO and C_2H_6 reactants mixture on a Pt/Al_2O_3 monolith. This is a practical problem encountered in the operation of Diesel Oxidation Catalyst.

The ignition temperatures of these two reactants are rather different. At a ramp rate of 1K/min a feed containing 1 % of the more reactive CO ignites at 460 K whereas a feed containing 500 ppm of the less reactive C_2H_6 ignites at 711 K. A feed temperature ramp of 10 K/min decreases each ignition temperatures by about 10 K. A mixture of these two reactants exhibits two separate ignition temperatures. Simulations reveal that a bifurcation diagrams showing the dependence of the difference between the exit solid and feed temperatures provide useful insight on the ignition of the CO and C_2H_6 mixture. An increase of the CO feed concentration by 1 % decreases the ethane ignition temperature by about 80 K. For a feed containing 3 % CO the ethane ignites at about K, which is very close to the ignition temperature of the CO. Thus, by increasing the concentration of the more reactive species with the lower ignition temperature, we can transform a separate to a simultaneous ignition. This insight may be utilized to destruct a rather unreactive environmental pollutant without using an excessively high temperature that may deactivate the catalyst.

ORAL PRESENTATIONS

Section II.

Chemical Reaction Engineering and Reactor Design – Novel Experimental Approaches, Modeling, Scale-Up and Optimization

AN EQUATION-ORIENTED APPROACH TO MODELING HETEROGENEOUS CATALYTIC REACTORS

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Mathematical modeling of diverse chemical processes can help to reduce experimental efforts during chemical processes development. Generally, two groups of mathematical modeling tools can be distinguished: block-oriented (BO) and equation-oriented (EO) approaches [1]. BO approaches address modeling on the flowsheet or reactor levels [2,3]. In the first case, every process is abstracted by a flowsheet consisting of the linked units, e.g. heat-exchanger, compressor, reactor, absorber, etc. In the second case, every reactor model is deconstructed into simpler objects such as reaction kinetics, thermodynamics, reactor geometry, reactor configuration, etc. Data are transferred between the individual objects. BO approaches have many advantages. However, reactor configurations are limited by a fixed set of reactors with given models and every unit or object is solved one by one in a predefined sequence. EO approaches have some advantages over the previous ones, for they support the implementation of more involved reactor models and simulators of EO process solve the system of equations simultaneously. The advantage last mentioned means that in comparison with BO, EO approaches are more flexible. Among equation-oriented approaches for reactor modeling one can distinguish such technique as computational fluid dynamics (CFD). CFD (commercial or in-house software) provide excessive data set with a limited physical meaning, too much experimental information is needed to validate CFD flow models. At present time, modeling and simulations that accurately treat both physics and chemistry of the real systems and parametrs independently obtained from measured or estimated data set are considered to be the most appropriate approach for modeling of many chemical reactors [4,5].

The purpose of the paper is to consider examples of application of such technique for modeling of heterogeneous catalytic reactors.

Multiscale mathematical modeling of tubular reactor. The main features of the reactor model are following: considering mass transfer processes inside the catalyst with taking into account pressure variation in the pellet; correlations for radial heat- and mass transfer parameters and wall heat transfer coefficients taking into account gas flow through holes in the pellets and between them. Scaling up chemical processes is performed after validation of mathematical modeling results by comparison with pilot scale experimental data [6-8]. Such processes as methane steam reforming, methanol oxidation into formic acid, selective ammonia oxidation to N_2O, phenol hydrogenation to cyclohexanone, β-picoline oxidation to nicotinic acid, oxidative dehydrogenation of ethane to ethylene, ect are considered in the paper.

Mathematical modelling of a fluidized bed reactor for propane-isobutane dehydrogenation has been performed on the base of a two-phase non-isothermal reactor model taking into account kinetics, convective transfer and axial gas-heat dispersion. Unique feature of the reactor is feeding of the regenerated hot catalyst into the top of the reactor thus increasing the reactor top temperature. The model is validated against output parameters of both pilot and industrial scale reactors [9].

Structured catalytic reactor with short contact time for partial oxidation of methane have been analysed by means of a dynamic one-dimensional two-phase reactor model with accounting for both transport limitations in the boundary layer of a fluid near the catalyst surface and detailed kinetics via elementary reactions. Simulation results are tested against available transient experimental data on the reaction ignition in a full-size monolith [10].

The examples considered in this paper show that the use of these models agree with the modern trends in chemical reaction engineering, such as [4,5,11]: an estimation of transfer coefficients with correlations which capture also the effect of reactor scale; simultaneous modeling transport-kinetic interactions on a catalytic particle scale and reactor scale; validation of the models against more than one output parameter and the data obtained under representative current process operating conditions. Efficient numerical methods with improved convergence have been developed to solve the systems of nonlinear equations. Both the method of lines and integro-interpolation method have been used to discretize the systems of PDEs and to obtain the systems of ODEs. The combination of iteration technique and a second-order Rosenbrock method was employed in solving these ODEs systems.

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OP-II-2

PROCESS INTENSIFICATION THROUGH LARGE EDDY SIMULATIONS OF TUBULAR REACTORS

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Light olefins are predominantly produced by steam cracking of hydrocarbons in long tubular reactors, suspended in gas fired furnaces. A limiting factor in the process is the deposition of cokes on the inner reactor tube surface, as this increases thermal resistance and pressure drop, which ultimately leads to production loss because the furnace has to be taken off-line for decoking.

Intensification of this process can be achieved by the introduction of 3D turbulators on the inside of the reactor, which is already applied industrially, e.g. MERT by Kubota [2], IHT by Lummus and Sinopec [3]. These turbulators aim at improving the radial mixing of the fluid and hence enhance the heat transfer, which implies a lower tube metal temperature (TMT) and consequently lowers the coking rate. The enhanced radial mixing also implies less radial gradients, resulting in a more uniform temperature and species distribution of the process gas as can be seen in Figure 1 (left).

On the downside, introduction of 3D elements is accompanied by an increased pressure drop over the reactor, leading to a loss of selectivity towards the desired products. Hence, implementation of these turbulators can be seen as a delicate interplay between an increased heat transfer and additional pressure losses. Hence, the design of these turbulators is not a straightforward task.

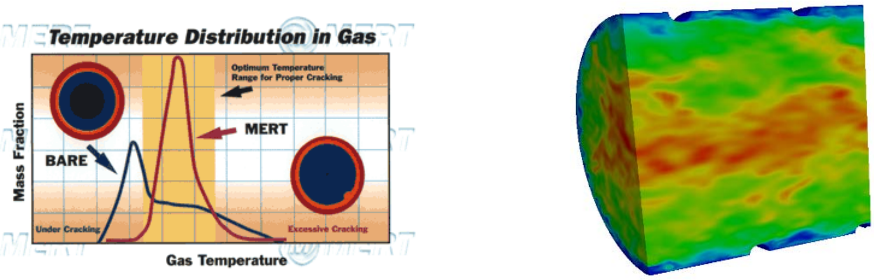

Figure 1: Improved temperature distribution in MERT[1] (left)
velocity flow field in MERT obtained with Large Eddy Simulations (right)

To gain deeper understanding on the influence of these 3D turbulators on the flow field, Computational Fluid Dynamics (CFD) is applied. Until today, completely solving the Navier-Stokes equationswith Direct Numerical Simulation (DNS) implies resolving turbulence on every time- and length scale, and is not feasible for industrially relevant conditions (Re > 50 000). To reduce the computational cost, Large Eddy Simulation (LES) offers a valuable alternative: the range of time- and length scales that are to be resolved is decreased by modelling the turbulence at the smallest scales and only resolving the larger eddies. This approximation is much more accurate than RANS, which models all the turbulent scales, making LES a better tool for the design and optimization of reactor geometries [4].

Even although LES has proven to be extremely valuable, it still requires modelling and the simulation accuracy is closely linked to the accuracy of the employed models. To assess the validity of these models, highly detailed experimental data was obtained thanks to a cooperation between the Laboratory for Chemical Technology (LCT) and the Von Karman Institute (VKI). Particle image velocimetry (PIV) and liquid crystal thermography (LCT) experiments were employed to determine velocity and temperature fields for industrially applied helically finned tubular reactors.

Thanks to this effort, a validated turbulence model is proposed and used to investigate the flow field in a range of tubular reactor geometries. Special attention was given to local flow patterns, local heat transfer and overall pressure drop as these parameters have a major influence on global and local coking rate and product selectivity.

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MODELLING MULTIPHASE REACTIONS IN A SINGLE CATALYST PELLET USING A DISCRETE APPROACH

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1. Introduction

In refining and chemical industries, multiphase catalytic reactions–including various hydrotreating and hydrocracking reactions–are of great importance. Despite this, the description of the processes within a catalyst pellet remains unclear.

This process consists of coupled mass transfer, reaction, capillary condensation, and pore blocking. Pore blocking may contribute to the complicated hysteresis phenomena observed in numerous experiments [1], but the level of importance of its contribution is still unknown. Furthermore, this process is affected by the pore network structure within a catalyst pellet, but this effect has not been systematically explored. This limited insight complicates the design of porous catalysts for multiphase reactions; to resolve this problem, a proper model is required.

A discrete model can describe pore blocking and the complex pore network structure, while a continuum model cannot [2]. Therefore, we propose a discrete model, which is experimentally validated. By using this model, we quantify the contribution of pore blocking to the hysteresis loop, and hereby probe the effect of the pore network structure on the hysteresis loop.

2. Discrete Model

The discrete model consists of three intimately coupled parts, namely: a three-dimensional pore network, diffusion and reaction, and phase change. The pore network represents the pore space of a catalyst particle, as illustrated in Fig. 1; the simulations of diffusion and reaction generate concentration profiles in the pore network, if phase distributions are provided; the simulations of phase change yield phase distributions in the pore network, if concentration profiles are provided. This model is based on the seminal work of Wood et al. [3]; the details of this model can be found in our paper [2].

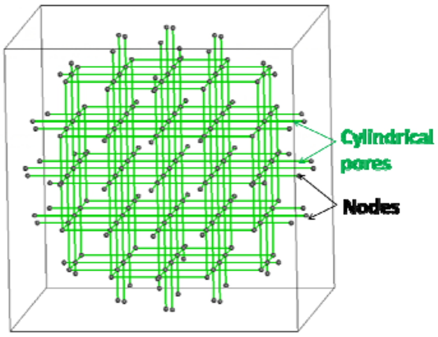

Figure 1. An illustration of three-dimensional, cubic pore networks (connectivity Z=6)

Hydrogenation of benzene to cyclohexane in Pd/γ-Al_2O_3 is used as the model reaction system, because of its industrial and academic importance.

3. Results and Discussion

3.1. Validation with Experiments

The discrete model is validated by comparing with experiments and a continuum model [1], as shown in Fig. 2. When changing bulk pressure of benzene in two different directions as indicated by the arrows, two branches for the effectiveness factor are observed, forming a hysteresis loop. The effectiveness factors calculated by the discrete model are much closer to the experimental ones, therefore, much better in describing hysteresis for multiphase reactions.

3.2. Contribution of Pore Blocking to the Hysteresis Loop Area

Fig. 3 indicates that 42 % of the hysteresis loop area is contributed by pore blocking. Pore blocking significantly affects multiphase reactions in catalysts, and, therefore, must be included in the models for these simulations. The discrete model can include pore blocking, but continuum models cannot, which also explains why the discrete model is much better in predicting experiments (see Fig. 2).

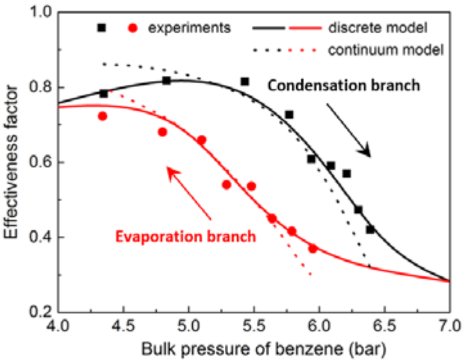

Figure 2. Comparison among the proposed discrete model (this work), a continuum model and experiments [1]

3.3. Effects of Bidisperse Pore Size Distribution on the Hysteresis Loop

A bidisperse pore size distribution is characteristic for the pore space of many real porous catalysts, which usually consist of micro/mesopores and macropores. So it also is for the Pd/γ-Al_2O_3 catalyst. The effects of two archetypical bidisperse pore structures, i.e., BD1 (a randomly spatial distribution of macropores) and BD2 (a cluster of macropores spanning the entire pore network), are compared, as shown in Fig. 4. The bidisperse pore structure significantly affects the hysteresis loop area (Sp) and the lower closure point (L), which can be explained by the theories of capillary condensation and pore blocking.

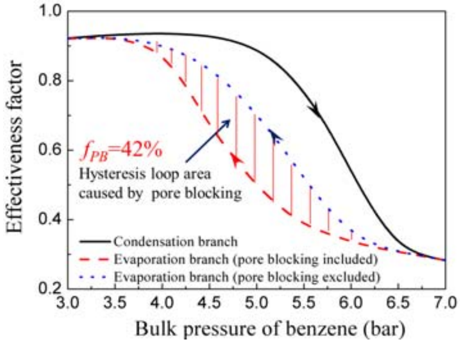

Figure 3. The percentage of the hysteresis loop area caused by pore blocking. The parameters used for simulations are taken from literature [2]

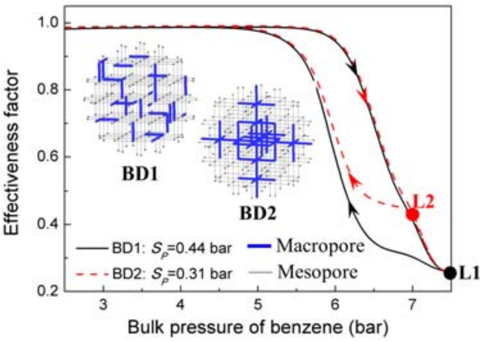

Figure 4. Effects of bidisperse pore structures (i.e., BD1 and BD2) on the hysteresis loop. The illustrations of BD1 and BD2 are shown in the insert

4. Conclusion

The proposed discrete model can couple mass transfer, reaction, capillary condensation, and especially pore blocking in a single catalyst. Therefore, this model can well describe the complicated hysteresis phenomena witnessed in experiments. By employing this model, many insights can be obtained that should serve the rational design of porous catalysts for multiphase reactions in gas/liquid/solid reactors.

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DIRECT SYNTHESIS OF DIMETHYL ETHER FROM SYNTHESIS GAS: EXPERIMENTAL STUDY AND MATHEMATICAL MODELING

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Dimethyl ether (DME) obtained through the stage of methanol formation from synthesis gas can be a very good substitute for conventional fuel and used as clean fuel or fuel additives for diesel engines. DME is produced from synthesis gas using two consequent reactors: the first reactor is used for methanol synthesis, while the second one is used for methanol dehydration to DME. Currently, the STD-process (synthesis gas conversion to DME) is extensively studied. In this case both reactions of methanol synthesis and its subsequent dehydration take place in a single reactor with interlacing of layers of catalysts used separately in two above mentioned processes [1]. This can shift the equilibrium and, thereby, intensify the process of DME synthesis.

The aim of the present work was to develop a kinetic model of the process of DME synthesis and mathematical modeling of the reactor.

To implement the STD-process a series of samples of catalysts, namely, Cu/Zn/Al methanol synthesis catalyst and γ-Al_2O_3 catalyst of methanol dehydration to DME, was synthesized. BET method was used to establish that in all synthesized samples mesoporous were formed with the size at least 0.3 cm^3/g, which is favorable for the process conduct, because the pore size should be sufficient for the penetration of hydrogen molecules (molecule diameter 0.35 nm), carbon monoxide (molecule diameter 0.32 nm), or carbon dioxide (molecule diameter 0.33 nm) into the internal pores.

The effect of such conditions as the catalyst loading (Fig. 1.), pressure, temperature, molar ratio of H_2/CO as well as the feed rate to achieve the optimal values of CO conversion and yield of DME were studied. The best loading found was charge with layer of mechanical mixture of catalysts for the synthesis and dehydration of methanol. Kinetic studies of the most active samples were carried out in a wide range of reaction conditions: contact time was 0.02-0.1 min, reaction temperature range was 220-280 °C, and component molar ratio were $CO:H_2 = 1:2$, 1:6, $CO:CO_2:H = 1:0,1:6$, P = 3 MPa.

The mechanism of interaction of H_2, CO, CO_2, CH_3OH and DME with surface of catalysts for the synthesis and dehydration of methanol was studied by TPD method with mass spectrometry. It was shown that the maximum rate of dehydration of methanol occurs on the surface of γ-Al_2O_3 catalyst with the formation of dimethyl ether at T_{max} = 280 °C, which is the optimal temperature for synthesis. The maximal values of CO conversion and DME yield were achieved at H_2/CO molar ratio of 1.

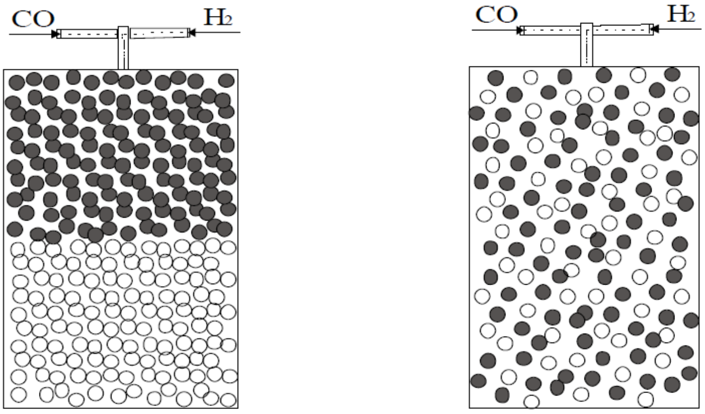

Fig. 1. Loading of catalysts for the synthesis ● and dehydration ○ of methanol

On the basis of experimental data and the results of physical methods research a kinetic model of the process of conversion of methanol to DME was developed, and model parameters were determined. The overall chemical reaction was the following: (i) the conversion of synthesis gas to methanol, then the subsequent conversion of methanol to dimethyl ether on ZSM-5, and finally the CO_2 formation by water-gas-shift reaction.

The mathematical modeling of a reactor was performed. It was shown that dimethyl ether synthesis in a single step on a CuO-ZnO-Al_2O_3/γ-Al_2O_3 catalyst allow significantly increases the yield of the desired product compared to the one obtained in two-reactor scheme.

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MODELING AND SIMULATION OF DEHYDRATION OF GLYCEROL TO ACROLEIN IN A FIXED-BED REACTOR

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Introduction

As a major by-product during the biodiesel production process, glycerol is formed in large quantities, and consequently with a low value on the market. It is therefore an important issue to find how to increase its value. One of the most interesting alternatives is to use it as a substitute for propylene in acrolein production [1]. More specifically, gas-phase dehydration is a very promising alternative and is widely investigated in the literature. However, very few studies are devoted to its kinetic modelling and measurements.

The aim of this work is to develop a phenomenological predictive model for the kinetics of glycerol dehydration to acrolein in a fixed-bed reactor. The model describes the phenomena involved in the reactor as well as reaction schemes and kinetic rates.

Reactor model

The glycerol dehydration to acrolein process includes two steps, dehydration and regeneration of catalyst. As the regeneration step is highly exothermic, a two-dimensional model was developed in a fixed-bed reactor. The same reactor model (two dimensional heterogeneous model) was used for the glycerol dehydration step although it is a low exothermic process.

Reaction scheme and kinetic model

The gas-phase dehydration of glycerol to acrolein involves several side reactions, among which the generation of coke could deactivate the catalyst. The impact of coke on the production of acrolein from glycerol has to be taken into account.

A heterogeneous surface coking deactivation model was proposed in this work. This model considers two types of active sites present on the surface of the catalyst. The reactions occur simultaneously on both sites which are both deactivated by coke. The activity of each catalyst site is proportional to its fractions of sites that are not occupied by coke.

The resulting process model equations were implemented and solved within gProms software, which is dedicated to dynamic simulation and optimization of processes. This software uses the Method of Lines to solve PDEs, and allows the choice of several discretization schemes and order of accuracies. The unknown parameters in the model were identified using the 'Parameter Estimation' tool of gProms. The objective function used was the maximum likelihood between experimental measurements and model predictions.

Results and Discussion

Several experimental measurements were carried out and used for the unknown parameters identification and model validation.

Among the numerous results obtained, Figure 1 presents experimental and simulated results for coke content evaluation with time and axial position of a lab-scale reactor. It shows that the kinetic model with heterogeneous surface deactivation gave a good fit to the experimental data for the formation of coke, not only as a function of time but also as a function of reactor length. The coke formation at the first two hours is much fast than the rest of time. The model with coke formation on two active sites with different rates predicts this evolution perfectively with meaningful physical interpretation of the kinetic parameters.

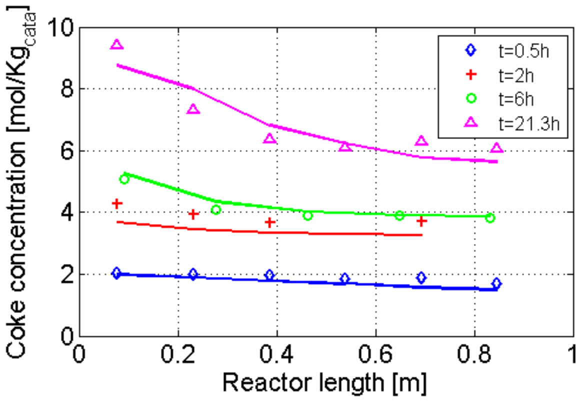

Figure 1. Evolution of coke content as predicted by the models and experimental data (dots: experiments, lines: simulations)

Conclusions

A two dimensional heterogeneous fixed-bed reactor model and a kinetic model for glycerol dehydration to acrolein process was set-up, identified and checked. Heterogeneous surface deactivation model was able to satisfactorily fit the experimental data with a meaningful physical interpretation of the kinetic parameters. The model was found to be accurate enough to predict the evaluation of coke content, catalyst activity and glycerol dehydration. The validation of model was carried out on both pilot-scale and lab-scale reactors.

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INERT MEMBRANE PACKED-BED REACTOR FOR PROPYLENE EPOXIDATION WITH HYDROGEN AND OXYGEN: MODELLING AND SIMULATION

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Propylene oxide (PO), as one of the most important chemical intermediates in petrochemical industry, is widely used in production of polyurethane and polyester resins. Compared to current production methods, the direct propylene epoxidation with oxygen and hydrogen is more competitive and attractive because it is simpler and more environmentally friendly. Recently, the performance, especially the activity and stability of the catalyst, has been significantly improved, which makes the catalyst commercially viable [1]. However, the reactor for this method should be carefully designed, because the gas mixture contains hydrogen and oxygen, in addition to propylene and propylene oxide, and is explosive in a wide range of composition.

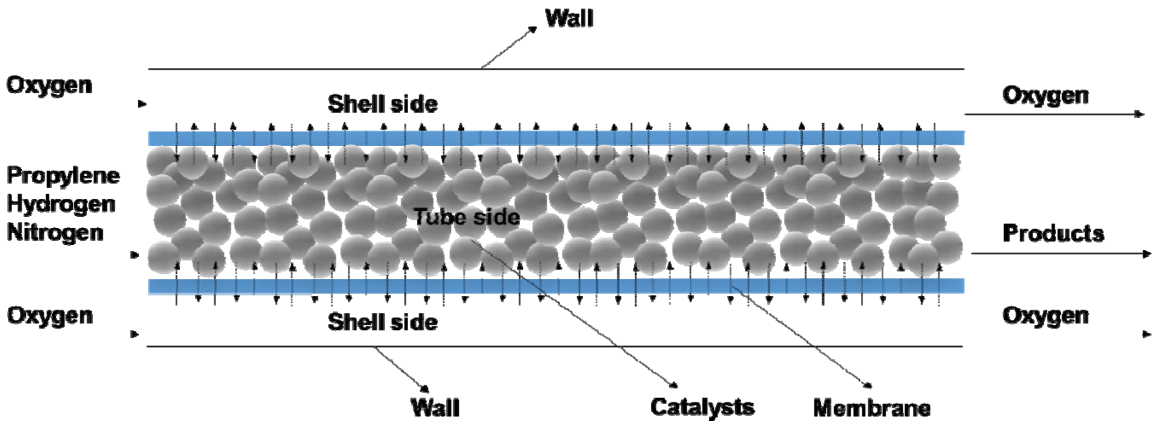

Fig. 1. Sketch of the inert membrane packed-bed reactor

In this work, an inert membrane packed-bed reactor (IMPBR) is proposed for this reaction, as shown in Fig. 1, to distribute oxygen feed and more importantly to prevent the formation of explosive gas mixture. Kinetics experiments were carried out on a gold catalyst with TS-1 as support. Kinetic equations were proposed and discriminated according to the apparent activation energy and reaction orders. The parameters of the selected kinetic expressions were then estimated by fitting the experiments.

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A two-dimensional pseudo-homogeneous model was developed for the inert membrane reactor to account for the two-dimensional flow and the gradient of concentration and temperature in radial direction. The effects of membrane permeability, and the operating condition on the conversion of propylene and selectivity to PO have been systematically investigated by simulation. The preliminary results show that the conversion can be significantly increased while maintaining the selectivity above a certain value, indicating clearly the merit of this membrane reactor configuration.

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PURE HYDROGEN PRODUCTION FROM ETHANOL AND GLYCEROL IN A MEMBRANE REFORMER

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This research is focused on understanding and developing scaled-down pure H_2 production schemes in Pd membrane reactors, through simulations and experimental campaign. Following studies of methane steam reforming (MSR) in a Pd membrane reactor packed with a catalytic-foam, which showed that high conversion and high hydrogen recovery can be achieved, we studied the process of ethanol SR in the same system. Full ethanol conversion is achieved with H_2, CO_2, CH_4 and CO as products. Separating H_2 directs the selectivity towards CO and CO_2, resulting also in increased CO to CH_4 ratios. In general, increasing temperature, pressure, and introducing sweep flow on the permeate side leads to better separation and higher permeate flow rates. In the above configurations the heat is supplied by an external heat source (electrically).

A mathematical model predicts the reactor's performance well, when membrane permeance is adjusted, but the apparent value is significantly lower than values measured in pure H_2. This is attributed to co-adsorbates. Concentration polarization effects are negligible as evident from a 2D model.

The design of an on-board autothermal membrane reactor producing pure hydrogen at atmospheric pressure is studied experimentally, with either methane or ethanol or glycerol as H_2 source. The design incorporates two reactors exchanging heat; an endothermic Pd-membrane-reformer, and an exothermic oxidation-reactor fed by the reforming effluents. The oxidation feed is distributed axially to avoid hotspots. The obtained performance of the 1.3 L system, with all feeds, is 0.15 kW (LHV) equivalent at an efficiency of ~25 %. The mathematical model, considering membrane permeance inhibition, is validated and used for optimization, showing that high efficiencies can be achieved in larger systems. This design serves as proof of concept for on-board pure H_2 generators, with flexible fuel source type, feeding an adjacent fuel cell.

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OP-II-8

INVESTIGATION OF INDUSTRIAL NH_3 OXIDATION BY COMPUTATIONAL FLUID DYNAMICS SIMULATIONS INCLUDING DETAILED SURFACE KINETICS

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Introduction

Heterogeneous catalytic oxidation of ammonia with oxygen on Pt/Rh gauzes is the first step of the Ostwald process. Motivated by large industrial importance there exist a big number of fundamental researches directed toward the mechanistic understanding of the process [1-3]. Despite numerous publications, there seems to be no published work that applies the existing reaction mechanisms in a flow simulation of the platinum gauze reactor. Since the reaction is known to be strongly heat- and mass transfer controlled, simulation which combine the surface chemistry, flow, diffusion and heat conduction are the key to the better understanding of the process and developing of new catalyst. In the last three decades the advent of the fast computers combined with the development of accurate numerical algorithms for solving physical and chemical problems allows us the performing of computational fluid dynamics (CFD) simulations on complex industrial catalytic gauzes with included detailed surface kinetics.

Results

A mechanistic model of ammonia oxidation on platinum previously published by Kraehnert and Baerns [3] was implemented in a CFD simulation using the rate mapping approach [4]. Simulations were performed for industrially used gauzes produced by Umicore. The main results obtained by the simulations can be summarized as follows

- Realistic temperature and concentration distribution in the model.
- The N_2O Selectivity varies along the perimeter of each wire. The front side of the wire has a higher selectivity as a rear side.
- Thicker wires show a lower N_2O selectivity than thinner wires.
- In a complex industrial gauze, the selectivity (Fig. 1) on the individual wires depends on the relative position of the wires in the gauze pack and is determined by local mass transfer effects.

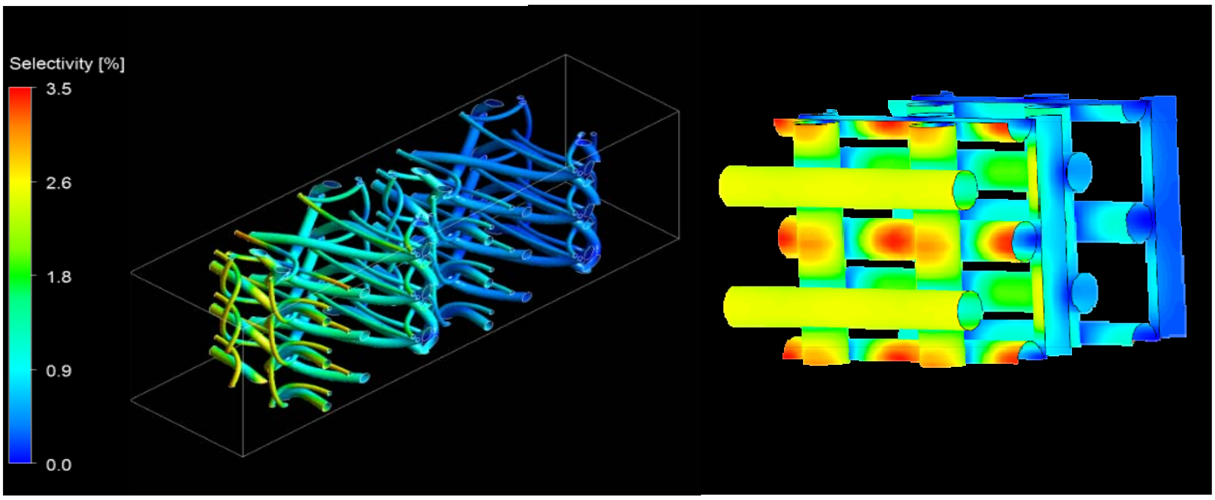

Fig. 1. The computed local N_2O selectivity in an industrial gauze (left) and woven gauze (right). The flow direction is from left to right. The absolute N_2O Selectivity is 1.4 % for industrial gauze (left) and 1.8 % for woven gauze (right)

Finally, the simulations have shown, that the complex industrial gauzes designs have lower N_2O selectivity compared to conventional woven gauzes. That aspect is in agreement with the industrial practice, where it has been observed that the conversion and selectivity is influenced by the geometry of catalytic gauze.

The current study provides for the first time CFD simulation coupled with detailed surface kinetic mechanism of ammonia oxidation on complex industrial gauzes. It can explain the observed influence of the geometry on the performance of the catalytic gauze. Furthermore that approach can be used for validation of other kinetic mechanisms and developing of new geometries for catalytic gauzes.

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OP-II-9

PREDICTION AND CONTROL OF INTERNAL TRANSPORT EFFECTS IN STRUCTURED AUTOMOTIVE EXHAUST GAS CATALYSTS AND FILTERS

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The increasingly strict emission limits for key pollutants in automotive exhaust gas (carbon monoxide – CO, hydrocarbons – HC, nitrogen oxides – NO_x, and particulate matter – PM) cannot be met without sophisticated systems of catalytic converters and particulate filters. Historically, particulate filters have been applied to Diesel engines that suffer from soot formation but the newly introduced limits on particulate numbers are going to enforce filters also for gasoline engines that produce small particles.

Both catalytic converters and filters are in the form of a cylindrical monolith with a large number of parallel channels in a honeycomb arrangement. The channels of catalytic converters are open and their walls are coated with a layer of active catalytic material where chemical reactions take place. In contrary, the filter channels are partially plugged so the exhaust gas is forced to permeate through the porous monolith walls, filtering out the soot and ash.

In addition to the development of more active and durable catalytic materials, the current efforts are focused on making the system of several catalytic converters and filter more compact and less expensive. This can be done by combing different catalytic materials in a single monolith with multiple coated layers (Figure 1a). In the case of filters, it is possible to apply the catalytically active material directly on or into the porous structure of the catalysed particulate filter (Figure 1b). In both cases, however, there are potential negative effects caused by internal transport limitations such as the hindered access of reactants to the bottom layers in multiple-coated monoliths, and an increase of pressure loss in catalysed filters.

In this contribution we present novel multi-scale models enabling to quantify the macroscopic performance of such structured devices (in terms of pollutant conversion, pressure loss etc.) depending on the morphology and location of the applied porous materials.

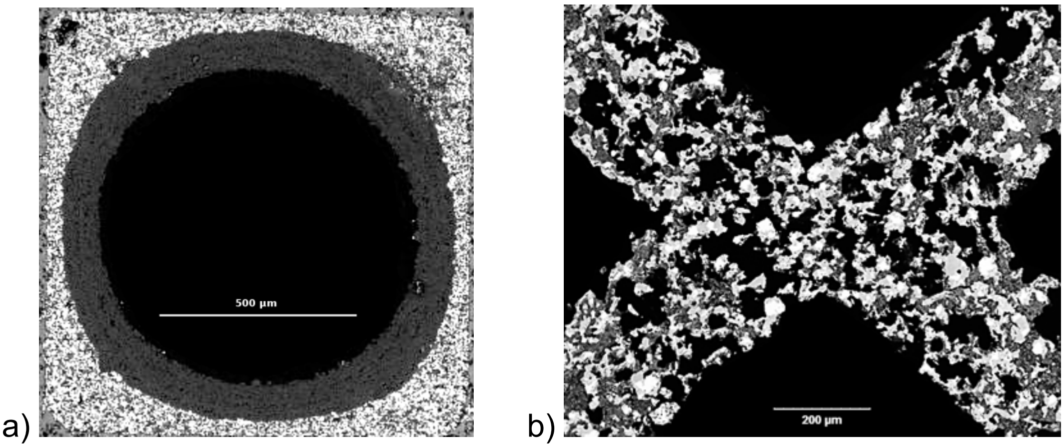

Figure 1. Cross-section SEM images of a) square monolith channel double-coated with two different porous catalytic layers (grey & white – catalytic materials, black – voids), and b) porous filter wall near the corner of adjacent square channels (white – wall material; grey – catalytic material inside wall pores; black – voids)

Several types of multi-layer catalytic monoliths (including alumina-based oxidation and lean NO_x trap layers as well as zeolite-based SCR layers) and filters are characterized by scanning electron microscopy, 3D X-ray microtomography and standard porosimetry techniques, covering the pore sizes from tens of microns to less than a nanometer. The morphology of samples is digitally reconstructed in 3D and used in micro-scale simulations of gas transport through the porous material [1, 2].

The obtained parameters, such as effective diffusivity and permeability, are then employed in a macroscopic model of monolith, enabling to simulate the performance of the entire device [1, 3]. The model predictions are compared with experimental data from lab reactor. The impact of transport limitations on the converter performance is evaluated for several different monolith configurations and key parameters that allow control of the material transport properties are discussed.

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OP-II-10

NATURE-INSPIRED FRACTAL FLOW FIELD FOR PEM FUEL CELLS

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One of the ongoing challenges faced by polymer electrolyte membrane (PEM) fuel cells for broader commercialisation is the accomplishment of uniform gas distribution across the catalyst layer. Ensuring reactant homogeneity is essential to improve fuel cell efficiency and to forestall adverse side reactions that are detrimental to fuel cell longevity [1]. Within the confines of the conventional flow fields, such as serpentine channels, this is an unavoidable consequence, due to reactant depletion across the channel [2]. This work aims to address the issue, inspired by the fractal geometry of the upper respiratory tract of the human lung as shown in Figure 1.

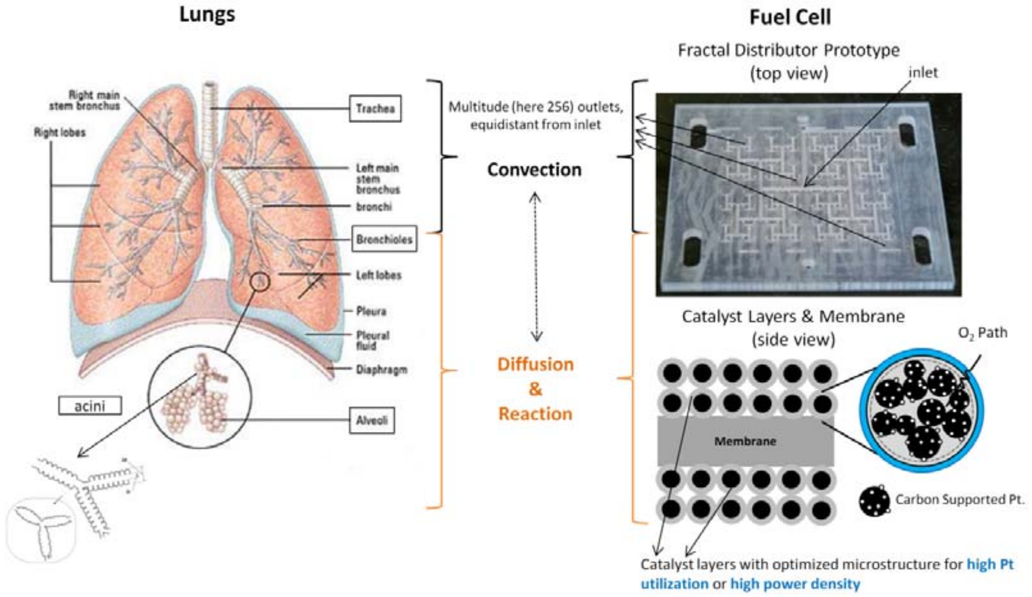

Figure 1. Flow field design inspired by the lung structure [3]. Image of lung courtesy of http://classes.yale.edu/fractals/panorama/Biology/Physiology/Physiology.html.

The human lung has been shown to have an optimal architecture that uniformly distributes oxygen from the trachea to the alveoli. Furthermore, the human lung transitions between two flow regimes: 14-16 upper generations of branches dominated by convection, and 7-9 lower generations of space-filling acini dominated by diffusion [4]. The upper generations of branches are designed to slow gas flow to a rate compatible with the rate in the diffusional regime (Pe≈1) [5] and the entropy production was found to be uniformly distributed in both regimes [4]. These characteristics that make the lung an optimal transport structure are all desirable for a PEM fuel cell.

The fractal pattern consists of repeating “H” shapes and by employing a fractal dimension of 2, where daughter “H’s” that are half the parent’s size, a plane filling geometry is attained. Furthermore, the three-dimensional branching structure allows only the outlets of the fractal inlet channel to be exposed to the MEA, eliminating the reactant depletion along the channel and providing uniform local conditions on the surface of the catalyst layer.

In this study, the reactant flow and cell performance were modelled for different numbers of fractal branching generation. Optimal performance was reached at a level of $N \geq 5$. Based on the simulation results, three fractal flow field prototypes were produced via selective laser sintering (SLS), a «3D printing» method, each representing a branching generation level of $N = 4$ and $N = 5$, and validated against a standard serpentine flow field. The results suggest improved mass transport for the fractal flow fields at high current density due to the homogeneous gas distribution. The fractal, $N = 4$ generation prototype demonstrated improved performance over the serpentine at all operating conditions investigated in this study and a good correlation with the results predicted by the model. The worse-than-expected performance of the fractal $N = 5$ generation prototype reveals insufficient convective liquid water removal due to the slow air velocity from each outlet. The findings elucidate the need for implementation of active water management systems to alleviate flooding, something we will briefly discuss as well.

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OP-II-11

NOVEL METAL-ENZYME CATALYST FOR ONE-POT DYNAMIC RESOLUTION IN A SPINNING CLOTH DISC REACTOR

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Imagine a reactor that could do a cascade of reactions without the need for product purification in between!

A large industrial problem with catalysts are that most are not compatible with each other and often several processing steps are necessary, including intermediate product purification and catalyst separation, both of which are expensive and energy intensive processes [1]. One novel approach (little researched but is starting to receive more academic attention) is to have a continuous flow across two or more catalysts spatially separated– i.e. single flow – multi catalysis, or continuous cascade chemistry [2].

Multi-catalyst, one-pot reactions find extensive application in pharmaceuticals where one enantiomer is more active and responsible for the necessary action of the drug and the other is less active and often causes adverse side effects [3]. The spinning mesh disc reactor (SMDR) is a novel technology and has the potential to augment this chemistry [4]. The SMDR uses centrifugal forces to allow an even spread of a thin film across a spinning horizontal disc covered by a replaceable cloth. The cloth can have a range of catalysts immobilized onto it, so as to have a series of reactions occurring in 'One-Pot' (Fig. 1). The aim of this study is thus to investigate and optimise the SMDR for cascade reactions.

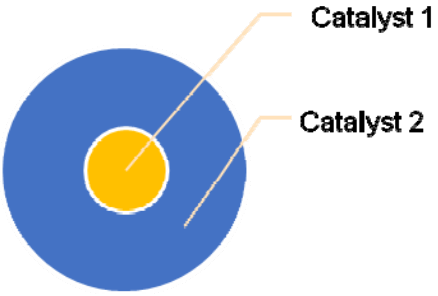

Fig. 1. Top view of spinning disc

Henry's reaction coupled with the kinetic resolution using copper triflate and lipase as catalysts was chosen as a model reaction to allow easy comparison to literature [3]. Wool was pre-treated with a solution of hydrogen peroxide and sodium silicate and modified with PEI. The modified cloth was rinsed with distilled water and soaked in copper triflate solution (in methanol) for 24 hours. Enzyme immobilisation was carried out by soaking the PEI modified cloth in lipase solution followed by cross-linking with glutaraldehyde. The cascade reactions were carried out in the SMDR by stacking the two different catalytic cloths on top of each other. The liquid firstly flowed through the cloth with the metal catalyst and then penetrated through to the enzyme immobilised cloth [5]. Reaction conversion was monitored continuously using NMR and HPLC. The effect of spinning speed, flowrate on conversion was also investigated. Conversion in batch (using both free and immobilized catalysts) and in the SMDR showed similar conversion of ~90 %, which were in agreement with literature [6]. However, the reaction time for the same conversion in SMDR was significantly shorter than the batch process, thus showing proof of concept and achieving process intensification.

To the best of the authors' knowledge, this is the first study that successfully has achieved a cascade reaction in a spinning disc reactor or in any kind of a similar reaction system. This further implies the huge potential in this area and we are currently investigating ways to further improve and optimise the reaction conditions in the SMDR.

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OP-II-12

FLOW CATALYTIC REACTORS FOR GAS-LIQUID CHEMISTRY: A $PdBi/TiO_2$-COATED MILLI-REACTOR FOR SEMIHYDROGENATION

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Fine chemicals industry produces a range of vital compounds from pharmaceuticals and nutritional products to agrochemicals and specialty fuels. Traditionally, these processes have been performed in batch reactors, that offer excellent versatility but have a range of technical and economic limitations. For example, slow heat transfer results in poor control of quick exothermic reactions, requiring either costly cryogenic conditions or excessive solvent dilution to avoid overreaction. Gas-liquid reactions such as hydrogenation, in particular, present an additional substantial safety hazard due to a large volume of explosive gas involved. Moreover, the interrupted nature of the batch process requires occasional stops, reactant/product changeovers and catalyst separation steps, increasing the labour costs. In this respect, flow chemistry technology offers attractive solutions allowing for cryo- and solvent-free reactions in intrinsically safe microreactors. The continuous nature of the flow processes decreases the labour costs.

Heterogeneously catalysed gas-liquid reactions, however, were very difficult to implement in flow micro- and milli- reactors until recently. The main challenges are scalability, difficulties to control the catalyst inside the flow reactor, and the product selectivity. In this work, we compare wall-coated capillary reactors that are based on our novel catalytic coating method[1] with batch reactors and a range of existing flow approaches such as catalyst slurry, packed-bed (PBR), and falling film microreactors (FFMR). The comparison is based on (i) the semihydrogenation kinetics of 2-methyl-3-butyn-2-ol (MBY) over a Pd/SiO_2 catalyst and (ii) the study of residence time distribution in these reactors. The semihydrogenation reaction selected provides a representative model system of a broad range of industrially important gas-liquid reactions used, for example, in vitamin A synthesis.

The results show that a slurry flow reactor is a close approximation of an ideal batch reactor allowing for accurate reaction timing and synthesis of intermediate products. However, the biggest problem in slurry is the subsequent separation, which is difficult even despite recent advances in magnetic separation or continuous filtering. Packed-bed reactors are widely used in gas-liquid petrochemical reactions, but their application in the fine chemicals synthesis provides substantial difficulties due to much a smaller scale and arising hydrodynamic problems such as gas-liquid channelling[2]. As a result of this, a precise control of the residence time is difficult resulting in poor yield of intermediate products and/or some reactant decomposition due to excessive contact with the catalyst. Moreover, the catalyst screening in these reactors is very difficult because not only catalyst chemical properties affect the product distribution, but the catalyst particle shapes and dimensions as well as packing density and wettability. Wall-coated reactors such as capillary and FFMR eliminate the hydrodynamic uncertainties, allowing for the synthesis of reaction intermediates. On the other hand, wall-coated reactors are less advantageous for the reactions with quick catalyst deactivation due to a difficult catalyst replacement compared to slurry reactors. Hence, wall-coated capillary reactors seem particularly promising for heterogeneously-catalysed gas-liquid reactions with minor catalyst deactivation because of scalability, low reactor costs and excellent reaction time control.

The concept has been studied in solvent-free MBY semihydrogenation in PdBi/TiO_2-coated capillary milli-reactors[3]. The maximum alkene yield of 90 % has been obtained in the coated reactor over the catalyst with a Pd/Bi molar ratio of 11. The capillary reactor coated with the PdBi/TiO_2 catalyst (Pd/Bi ratio of 7) allowed for maximum alkene yield of 95 %. The same yield has been obtained in a batch reactor where no mass-transfer limitations were observed. This result experimentally demonstrates that the reaction intermediates can be obtained in capillary milli-reactors with the same yield as in an ideal batch reactor.

The PdBi/TiO_2 catalyst has been studied in solvent-free MBY semihydrogenation for 100 h on stream and substantial leaching of Bi was observed leading to the decrease in alkene selectivity from 98 to 92 %. The leaching was successfully supressed adding 1 vol. % acetic acid into MBY feed resulting in a constant selectivity of 98 % for 100 h on stream. This result suggests that the main reason of Bi leaching is associated with its oxidation by the reaction with impurities such as dissolved oxygen or moisture, which is efficiently supressed in acidic conditions.

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OP-II-13

BEAD SIZE DISTRIBUTION CONTROL OF THE EXPANDABLE POLYSTYRENE PRODUCTION WITH SUSPENSION POLYMERIZATION

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Polystyrene has been used in daily life for many purposes such as insulation boards, roofing materials, and decorative articles, or carry-out food packaging, refrigerant containers, industrial packaging, disposable trays, plates, cutlery, bowls and cups, or parts in white goods. Commercially there are three main types of polystyrene that is used in industry: General Purpose (GPPS), High Impact (HIPS) and Expandable Polystyrene (EPS). Commercially polystyrene is produced with two main polymerization processes: One is known as mass polymerization, which is a combination of continuously stirred tank and plug flow reactors in series. By this process, GPPS and HIPS granules are produced. The other process is known as suspension polymerization which is composed of a batch type reactor. Spherical EPS beads are mainly obtained by suspension polymerization process. Unlike mass polymerization, suspension polymerization is much harder to control due to the suspension stability which is strongly dependent on the reactor geometry, agitation conditions, temperature control and the effect of different additives such as suspension agents, polymerization initiators, and particle morphology stabilizers. Otherwise, even small changes within the system may lead to suspension failure which is unwanted due to loss of money and time to clean the reactors for EPS manufacturers. Therefore, a careful control of system parameters by temperature changes, feed rates, agitation conditions and viscosity changes during the production are of crucial importance. Apart from suspension failures, especially an important issue during industrial production of EPS is the control of particle size distribution since different size ranges of EPS beads are used for different purposes (construction or packaging) and hence obtaining broader particle size distribution is primary purpose for many EPS manufacturers [1,5]. In this study, the particle size distribution was tracked due to changing reactor geometry and agitation conditions. EPS beads were produced with two different laboratory scale glass reactors with the same formulation which was obtained from industry to give insight for industrial production as well. Drastic changes in particle size distribution were observed due to reactor geometry and agitation conditions as can be seen in Figure 1.

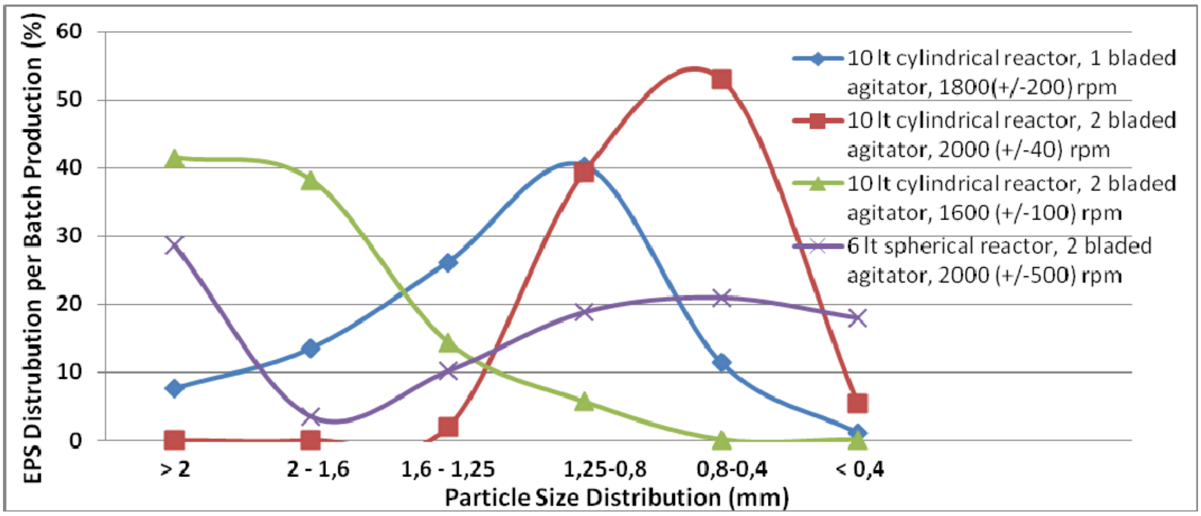

Figure 1. Particle size distribution of EPS beads depending on reactor geometry and agitation conditions

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AN ANNULAR LED-BASED REACTOR FOR PHOTOCATALYSIS APPLICATIONS: MODELING AND EXPERIMENTAL VALIDATION STUDY

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Heterogeneous photocatalysis is attracting much attention due to its large number of applications including air and water purification [1, 2], water splitting [3], and conversion of carbon dioxide to valuable hydrocarbons [4]. Nevertheless, its commercialization has been hindered by the low overall efficiency of the process [5]. One of the main challenges is to overcome the poor photon utilization within a photocatalytic reactor, which leads to high operational cost.

The rate of photocatalytic reactions depends typically on both the concentrations of the chemical species and the rate of photon absorption by a catalyst [6]. Thus, investigation of the radiation field within the reactor is crucial for improved reactor design, optimization, and scale-up. Conventional UV-lamps such as low pressure mercury lamps restrict the reactor design due to their large rigid design. Moreover, fragility, toxicity, gas leakage and disposal issues are other disadvantages of mercury lamps [7]. Alternatively, Light Emitting Diodes (LEDs) are promising light sources for photocatalysis applications [8-10]. LEDs are robust, energy-efficient, non-toxic and long lasting light sources. In addition, LEDs can be placed flexibly within each reactor configuration due to their small size and ability to deliver a range of intensities, which provides a large design space. To systematically exploit this enlarged design space, analysis and optimization of models for novel LED-based photocatalytic reactors is needed in combination with the validation of such models.

The objective of this study is to validate a model that describes the operational performance of a LED-based photocatalytic reactor. A mini-pilot plant involving an annular photocatalytic reactor using LEDs has been designed and constructed (see Figure 1). The LEDs are mounted on an inner concentric tube of the reactor. The position of the LEDs can be adjusted to modify the radiation field inside the reactor. Toluene degradation was chosen as the model reaction. The radiation field from the LED assembly was modelled and coupled with a reactor model involving mass, momentum and radiation transport balances. The model allows for kinetic parameters to be estimated from experimental data. Furthermore, the experimental setup allows for different flow rates, toluene inlet concentrations, methods for catalyst coating (hydrothermal method and atomic layer deposition) and light intensities to be applied to validate the predictive capabilities of the developed model for a broad range of operating conditions. On the long term, the validation of the proposed model advances the design, optimization and scale-up of future LED-based photocatalytic reactors for various applications.

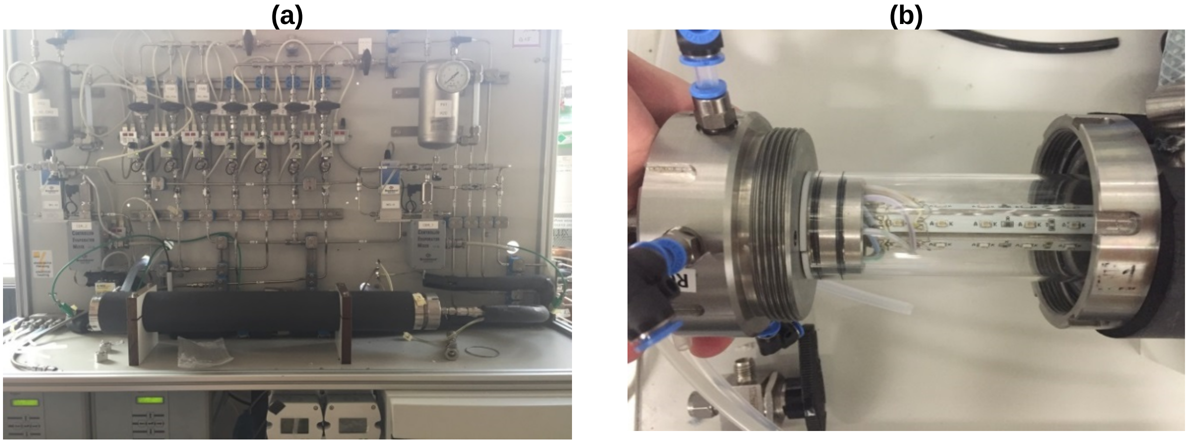

Figure 1: a) LED-based photocatalytic reactor setup, b) LED-based photocatalytic reactor including three concentric tubes: the inner tube for mounting LEDs, the middle tube of quartz for separating reaction medium from the light sources and the stainless steel reactor shell with catalyst coating.

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OP-II-15

PLASMA NITRIC OXIDE PRODUCTION AT ATMOSPHERIC PRESSURE IN PULSE POWER DRIVEN MILLI-SCALE GLIDING ARC PLASMA REACTOR

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The abundantly available nitrogen cannot be readily accessed without fixing it with either oxygen or hydrogen. Fixed nitrogen is useful for many industrial applications ranging from HNO_3 to HCN. The commercial process to fix nitrogen is the Haber-Bosch process, which is favored by high pressure and temperature operation, it consumes ~1 % of world's total energy production and 2-3 % of total natural gas output [1,2].

The most simple and promising route of chemically fixing nitrogen is to combine it with oxygen, which needs 3 times lower theoretical energy than that of H-B process. However, the major challenges is to supply high dissociation energy for nitrogen (9.7 eV). This challenge can be overcome by employing plasma as an alternative energy source and non-thermal gliding arc reactor, which helps to fix nitrogen at atmospheric pressure and at low temperatures [3,4].

$$N_2 + O_2 \xleftrightarrow{Plasma} 2NO \qquad \Delta H = 90\frac{kJ}{mol} \approx 1eV$$

The gliding arc reactor is operated at higher frequency (kHz) and powered with nano-second pulses. The reactor is made of Macor® and consists of 2 thin diverging knife-shaped tungsten electrodes with thickness of 2.5 mm and discharge gap of 2 mm [5].

Figure 1 shows the typical V-I signal for power pulses, the effect of specific energy input (SEI) and feed ratio on NO_x concentration. NO_x concentration found to increase linearly with SEI. Lower flowrates was found to yield highest NO_x concentration. Air and air + 35 % O_2 produced higher NO_x concentration than the N_2-O_2 mixture. Addition of argon and preheating of feed was found to have negative impact on the gliding arc ignition, thus resulted in decreased NO_x concentration.

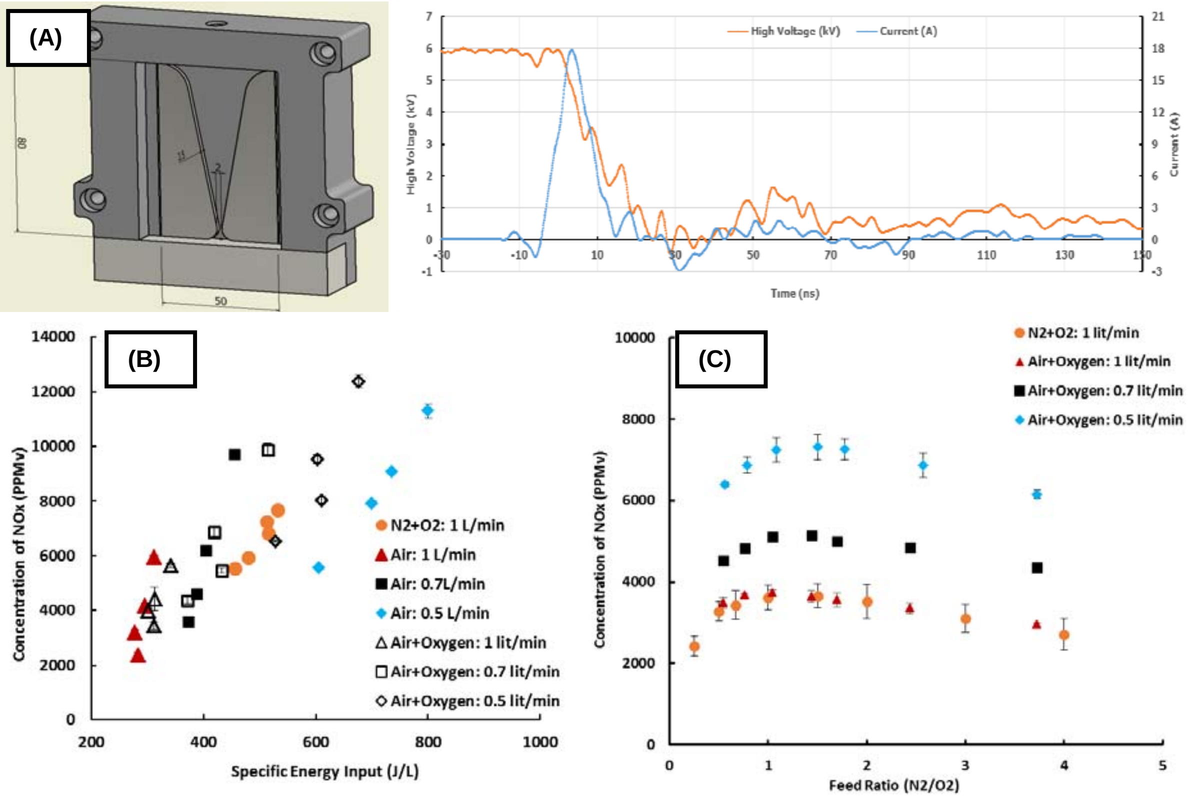

Figure 1. A. Milli-scale gliding arc reactor with V-I curves for power delivered ns, effect of **B.** flowrate, **C.** feed ratio on NOx synthesis

The performance of milli-scale gliding arc reactor powered by the nano-second pulses is investigated for nitric oxide synthesis at atmospheric pressure. The milli-scale gliding arc reactor could produce around 1.3 vol % of NO_x with high energy efficiency i.e. 1.1 MJ/mol. Feed ratio from 1 to 1.5 was found to be the optimum feed ratio for higher NO_x production. Argon addition and feed preheating shown a negative impact on the NO_x production. A thorough understanding of the NO_x plasma chemistry would be developed by building a 0D model of NO_x chemistry.

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OP-II-16

ENERGY AND EXERGY ANALYSES OF SORPTION ENHANCED CHEMICAL LOOPING REFORMING PROCESS FOR HYDROGEN PRODUCTION FROM GLYCEROL

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Hydrogen is one of the most important raw materials in chemical industries and also considered as a clean energy carrier that can be used as fuel in fuel cells to generate electricity without releasing carbon dioxide. Although the global hydrogen consumption is increasing rapidly, the majority of hydrogen is originated from depleting fossil fuels. Regarding the aspect of sustainability, interest in hydrogen production process inside of renewable fuels has been received attention. While the adoption of biodiesel continues to proceed worldwide, glycerol; which is a major byproduct from biodiesel production via a transesterification process, is glut the market. To meet the growing demand of hydrogen and utilize a valuable excess of glycerol, it reveals a promising way to bridge the gap by using the glycerol for hydrogen production [1].

Glycerol can be reformed into hydrogen by different methods, e.g., steam reforming process, partial oxidation gasification process, auto-thermal reforming process, aqueous-phase reforming process and supercritical water reforming process. Recently, the sorption enhanced chemical looping reforming (SECLR) which combines a chemical looping reforming method (CLR) and a sorption enhanced reforming method (SER) in one stage process has been proposed [2]. The chemical looping reforming method is used for the production of hydrogen via cyclic reduction and oxidation of a solid oxygen carrier, whereas the sorption enhanced reforming method with in-situ CO_2 removal is employed for production and enhancement of high purity hydrogen. This process can produce high purity H_2 without need for additional gas separation equipment. However, most of the studies were focused on the effect of parameter for process investigation, less work has been done on energy and exergy analyses of sorption enhanced chemical looping reforming process for hydrogen production from glycerol.

In the present paper, the first and second laws of thermodynamics are applied to a hydrogen production system in order to investigate changes in the SECLR process.

The energy usage in three interconnected fluidized bed reactors, i.e., reforming reactor, calcination reactor and air reactor, and the irreversibility resulting from various chemical reaction sets are studied. Energy and exergy efficiencies and exergy destruction of optimal process for hydrogen production from glycerol were also compared and discussed.

The energy and exergy analysis of the SECLR process are performed to analyze process performance and identify the sites having exergy losses as shown in Table 1. The designed SECLR provide the energy and exergy efficiencies of 79.79 % and 75.11 %, respectively. The majority of exergy destruction in the SECLR process occurs in the reforming reactor due to the high irreversibility of chemical reaction. When compare energy and exergy efficiencies of the SECLR with conventional processes [3-4], it found that the SECLR provides higher energy and exergy efficiencies than the conventional process. Therefore, the SECLR process has capable of improving the performance of the hydrogen production process.

Table 1. Energy and exergy efficiencies and exergy destruction of optimal process for hydrogen production from glycerol

Process	Efficiency (%)		$Ex_{destruction}$
	Energy	Exergy	(kJ/mol H_2)
SECLR (This work)	79.79	75.11	86.68
Steam Glycerol Reforming: SGR [3]	66.60	59.90	151.45
Glycerol Autothermal Reforming: ATR [4]	66.60	57.03	152.00

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OP-II-17

MODIFICATIONS OF THE ADSORPTION-CATALYTIC SYSTEM FOR ORGANIC IMPURITIES REMOVING

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Removal of volatile organic compounds (VOCs) from industrial waste gases is an important problem of atmospheric air protection. In the case of diluted gases it is expedient to use thermal and catalytic oxidation of VOCs with oxygen to carbon dioxide and water vapor. The treatment of atmospheric emissions with impurities of very low concentrations (below 0.1 g/m^3) is a serious problem since it requires an additional energy input. Adsorption-catalytic processes based on adsorption of VOCs directly on the surface of deep oxidation catalysts at low temperature with periodic regeneration of the catalyst by oxidation of the adsorbed impurities at elevated temperatures are of particular interest in this problem. However, their disadvantage is a partial desorption of non-oxidized VOCs during heating of the catalyst that leads to some reduction of the purification degree [1].

This study is devoted to the catalyst bed modifications for reduction of the energy consumption and maximal VOCs concentrations in outlet gas during regeneration.

Reducing of energy consumption is achieved due to disposition of the heater directly in the inlet part of the catalyst-adsorbent bed. During the catalyst heating the adsorbed VOCs start to oxidize with heat release, forming a heat wave that expands in all directions due to the heat conductivity. And the process proceeds in the autothermal regime, which allows to minimize the energy consumption. More over, the process may be realized in a continuous mode using unpurified inlet gas as a regenerating flow.

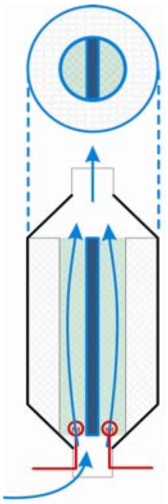

Fig. 1. Reactor with 2 sections

Reduction of the emission of VOCs during the regeneration may be provided by division of the catalyst bed into parallel non-inter-connected sections in the plane along the gas flow moving (Fig. 1). Each of these sections has an independent heater, and the inlet flow is divided between all sections. The regeneration is performed in all sections by turn. The outlet flow of regenerating section mixes with the flows from the other sections. Such mixing minimizes the peak concentration of desorbed VOCs and maximal temperatures in total outlet flow.

The proposed theoretical technological improvements of adsorption-catalytic bed were confirmed by the pilot tests in 2-liter catalyst bed with styrene and toluene in feed air. The experiments with inner heater (Fig. 2) were performed with lean styrene gas (55 ppm styrene in air). The purification degree in these experimental series with styrene was as high as 97-99 %. The 1- and 2-section comparison experiments (Fig. 3) were performed with toluene (~100 ppm). It is seen that the outlet gas temperature is about 2 times lower in 2-section reactor.

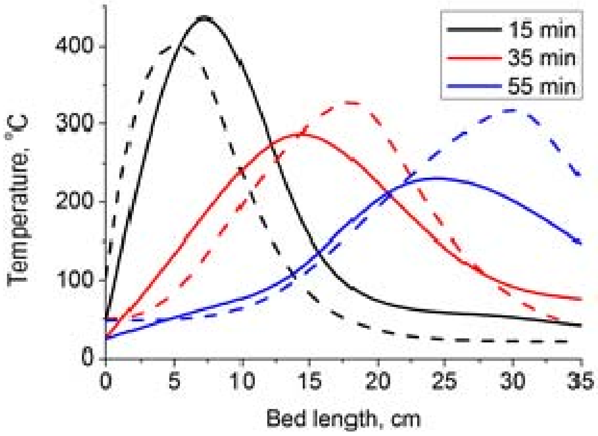

Fig. 2. Experimental (solid) and simulated (dashed) temperature profiles along the reactor axis

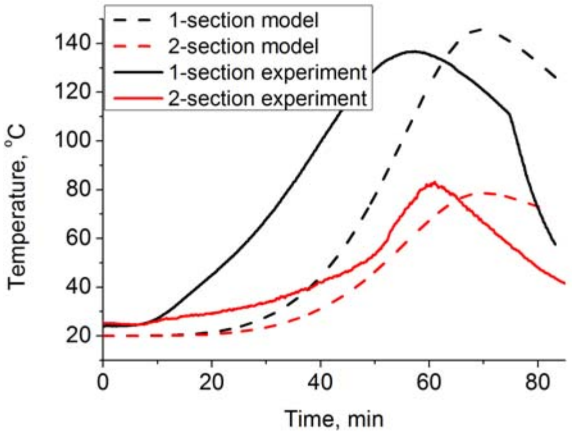

Fig. 3. Experimental (solid) and simulated (dashed lines) outlet temperature for 1- and 2-section reactors

The experiments were also simulated using the mathematical model proposed earlier in [2]. Fig. 2 and 3 show a rather good agreement between model and experimental time variation of the temperature profiles.

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OP-II-18

MODELING MOVING REACTION FRONTS DURING THE TRANSIENT VOC (TOLUENE) OXIDATION IN A PACKED-BED CATALYTIC REACTOR

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A model is developed aiming to study the transient behavior of a non-isothermal, non-adiabatic packed-bed reactor during VOC (toluene) oxidation with air on a mixed-oxide catalyst, using a Mars-van Krevelen kinetic scheme, when concentration and temperature at the feed vary periodically in a sinusoidal way with time-on-stream. In this case the feed of air containing toluene comes from a batery of adsorption units that recovers VOC components from very dilute streams. Once each batchwise operated adsorption column becomes saturated, a non-isothermal desorption should take place, and the exiting gas stream from each adsorption column is the feed to the catalytic reactor for VOC elimination, that should operate continuously. The reactor is given by a 2D two-phase transient model that includes axial and radial dispersion of heat and mass. The oscillatory behavior of this class of reactors to perturbations in temperature and concentration at the feed have been experimentally verified [1,2] for the oxidation of carbon monoxide on Pt/Alumina catalyst, and theoretically described [3]. The observed behavior from our simulations shows that traveling reaction fronts exist in the packed-bed for selected feed conditions, however they change in nature according to the balance achieved between the transients in heat generation and heat elimination depending on the magnitude of the flow velocity, as it has been demosntrated before [4]. Two cases are analyzed (shown in Figs. 1 to 4), for the periodical variations in a sinusoidal way of the feed conditions around its nominal value (To = 200 °C; C_{AO} = 0.35 mole % in air), for a gas flow rate: 500 cm^3/s (STP) and reactor diameters: 1.5 and 2.0 cm. Figures 1 and 3 show the sinusoidal variations in temperature and concentration (same amplitud but different period) at the feed for the two cases, and the corresponding oscilatory response of the temperature at the reactor´s exit, with different amplitud and period. Figures 2 and 4 show the corresponding transient reactor responses in terms of the traveling axial temperature profiles, at a time marked as the last transient in Figs. 1 and 3. The transient responses from t = 0 to 4600 are not shown. For the same gas flow rate but different reactor diameters, the different gas velocities produce transients in which heat elimination and heat generation are balanced in a different way in each reactor, affecting the way temperature (reaction) moving fronts are produced, as observed on Figs. 2 and 4.

Fig. 1

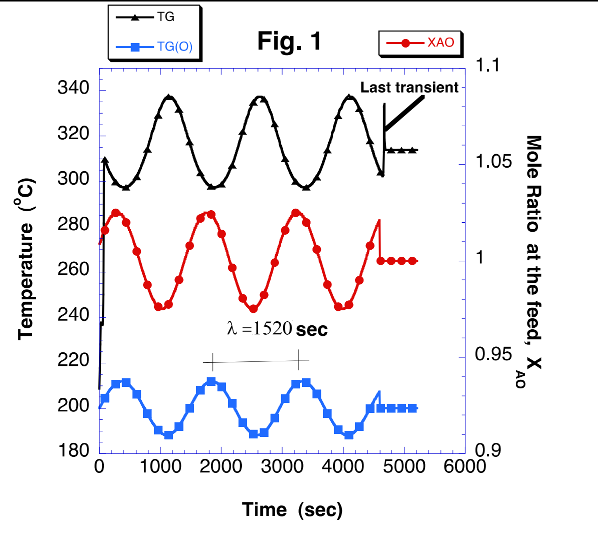


Fig. 2

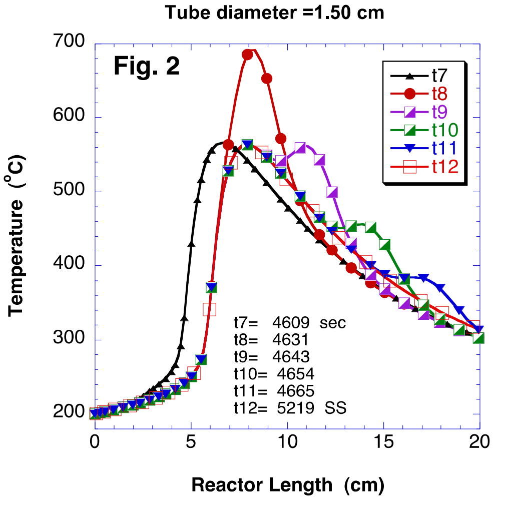


Fig. 3

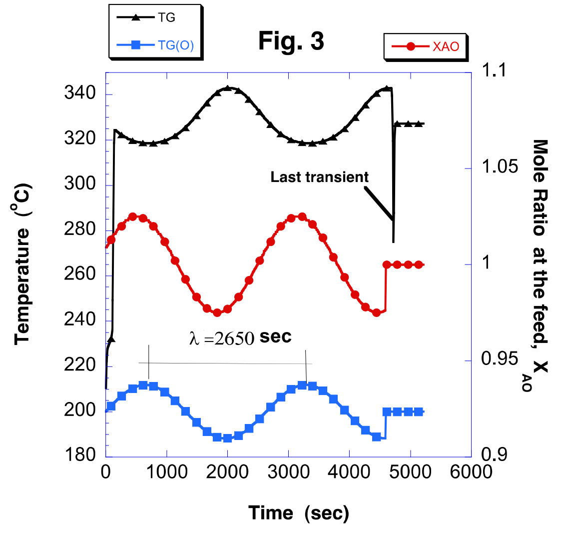
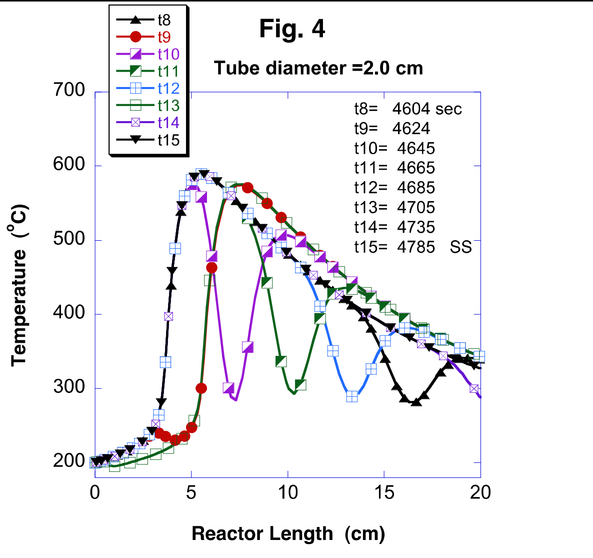


Fig. 4



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ORAL PRESENTATIONS

Section III.

Chemical Reactors and Technologies for Targeted Applications

JOINT CONTINUOUS SYNTHESIS AND PURIFICATION OF ARTEMISININ AND ARTESUNATE

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It was shown recently, that for the efficient production and purification of a model compound the outlet of a flow reactor could be successfully fed directly into a simulated moving bed (SMB) chromatography unit in order to carry out the reaction and separation processes continuously [1, 2].

Artemisinin, contained in sweet wormwood, and its derivatives β-artemether, β-arteether and α-artesunate are currently the basis for the most effective ways to cure the malaria disease [3]. Effective continuous photocatalytic synthesis of artemisisin in a laboratory flow reactor from the waste product dihydroartemisinic acid was reported recently [4, 5]. The possibility of further synthesizing the mentioned derivatives also in a continuous way was demonstrated for artesunate [6].

We will present selected results from a collaboration of our group with the group of Peter Seeberger (Max Planck Institute for Colloids and Interfaces, Potsdam-Golm). Different scenarios of the continuous production and isolation of artemisinin and artesunate will be in the focus of the lecture. One of the investigated options is based on applying a 3-zone open-loop SMB process with an additional regeneration zone [7].

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OP-III-2

KINETIC MODELING OF (+)-NOOTKATONE BIOCONVERSION

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Keywords: *Hydrodynamics, Kinetics, Stirred Tank Reactor, (+)-Nootkatone Bioconversion*

Multiphase partitioning bioreactor conception seems to have a great potential in enhancing the productivity of (+)-nootkatone from the oxidation of (+)-valencene contained in orange essential oil using *Yarrowia lipolytica*. Nevertheless, independent studies of transport phenomena and kinetics are essential to have a successful scaling-up of this bioreactor concept. In this work a pseudo extrinsic kinetic model based on elementary reactions for (+)-valencene oxidation to (+)-nootkatone is developed. The kinetic study is conducted in a 1000 mL batch stirred tank reactor (STR) containing an aqueous phase, (+)-valencene and *Yarrowia lipolytica*, and a gas phase to feed the oxygen necessary for the bioconversion.

Firstly, the role of hydrodynamics on mass transport in absence of bioconversion is assessed. Particularly, velocity field from the gas phase and aqueous phases is determined using CFD in general, and κ-ε turbulence model and bubble model, respectively, in particular. Thus, hydrodynamics from both aqueous and gas phase in the STR is coupled to the oxygen mass transport model accounting for convective, dispersive and interfacial phenomena. From this end, local interfacial mass transport coefficients are determined, and are integrated to obtain the corresponding effective parameter that accounts for the role of hydrodynamics on mass transport in some detail. Secondly, this information is transferred to the classical bioconversion model that describes bioconversion experiments, and accounts for oxygen mass transport from the gas to the aqueous phase along with biorreaction. The reaction mechanism proposed follows the formalism of Langmuir-Hinshelwood and considers cell viability deactivation. Approximations of the pseudo equilibrium of reaction rates or steady state intermediary species are not considered, thus, identifying the role of each reaction step involved in the bioconversion.

The reactor model and proposed methodology adequately describes the observations with and without bioconversion. Because space constrains graphical results are no presented herein. The regression and the estimated parameters are statistically significant, making these analyses reliable regarding the kinetic behavior of *Yarrowia lipolytica*. The affinity and inhibition constants of substrate and oxygen are obtained and discussed from the kinetic parameters of the model.

OP-III-3

EXPERIMENTAL AND NUMERICAL INVESTIGATION OF HYDRODYNAMICS AND MIXING IN A DUAL-IMPELLER MECHANICALLY-STIRRED DIGESTER

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Biohydrogen ($BioH_2$) from agriculture and lignocellulosic waste appears as a serious alternative to conventional fuels; it is considered as an ideal vector and a clean energy for sustainability. 2nd generation $BioH_2$ can be obtained through acidogenic fermentation, an anaerobic digestion process that couples the treatment of organic waste to renewable energy production. Mixing plays a key role in this process, as a three-phase system is involved: namely, an aqueous solution enriched in soluble sugars and fatty acids, a suspended lignocellulosic waste and a gas phase composed of CO_2 and H_2. Agitation must enable the suspension of organic waste, homogenize pH and local concentrations, and enhance hydrogen desorption at the same time[1], but agitation intensity is limited because shear stress may impair the biological processes. The aim of this work is, therefore, to investigate the influence of mixer design and operating conditions in an anaerobic digester designed for $BioH_2$ production, so that critical limiting factors, e.g. insufficient mixing, inhomogeneous nutrient distribution, and slow gas-liquid mass transfer, may be identified early in the design process.

To analyze the effect of the mixer design both on hydrodynamics and mixing, experiments were conducted in a laboratory-scale unbaffled, round-bottomed, 5-L mechanically-stirred tank bioreactor. Mixing was investigated through different dual-impeller configurations with various impeller size, clearance and types: namely, marine propeller, elephant ear impeller, and Rushton turbines with 4 and 6 blades, respectively. Advanced optical experimental techniques, such as Particle Image Velocimetry (PIV) and Planar Laser Induced Fluorescence (PLIF) were used to determine mixing time t_m and the flow pattern in the bioreactor. PLIF, decolorization and conductimetric methods were compared for mixing analysis. Experimental results were confronted to CFD data obtained using a commercial software package (Phoenics®, *Cham Ltd.*, *UK*) for which the closure, boundary and simulation conditions defined in a previous work[2].

The experimental results suggest that mixing conditions can be strongly modified by small changes in the configuration and clearance of the dual-impeller device, and by rotation speed, as vortex formation may arise when this is above 150 rpm. Below this value, power input is between 5-10 W/m^3, which is in agreement with US EPA recommendation for anaerobic digestion sustainability[1]. First, t_m strongly varies with the position of the injection point of the tracer, and values derived from the conductimetric technique can be higher than those deduced from chemical decolorization when the conductimetric probe is placed vertically between the impellers. This behavior can be explained by an evolution of the flow pattern, highlighted by CFD simulations and validated by PIV data, as a function of the distance and the diameter ratio between impellers. For example, the radial flow expected with a Rushton turbine in the bottom region can be overshadowed by an interaction with an elephant ear impeller in the top region, leading to an overall circulation which enhances at the same time solid suspension and vortex formation. Conversely, three-cell and four-cell patterns can also be observed even when a marine propeller is used as the bottom impeller. As a result, t_m can vary by a factor 2-3 with small changes in impeller design, while power input and the onset of vortex formation are less extensively modified, and mass transfer evolution deduced from oxygen desorption experiments is weak.

As a conclusion, mechanically-stirred digesters are driven at low power input for economic sustainability, so that the strategy for impeller design must be revised. When solid waste has to be handled and BioH$_2$ production is the objective, a dual-impeller configuration is adequate to avoid settling, and to enhance liquid-to-gas mass transfer at the same time. Actually, flow pattern and mixing time are shown to be strongly affected by small changes in impeller size, diameter and clearance. Consequently, CFD emerges as a versatile tool to predict these flow patterns and detect the presence and position of dead zones that could not always be detected by chemical decolorization.

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OP-III-4

FAST PYROLYSIS OF LIGNOCELLULOSIC BIOMASS IN THE GAS-SOLID VORTEX REACTOR

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The Gas-Solid Vortex Reactor (GSVR) enables fluidization in a centrifugal field with forces that exceed the gravitational force multiple times. A dense and uniform bed of particles with bed width-to-height ratios and gas-solid slip velocities much higher than in conventional fluidized beds can be sustained [1]. Due to the increased bed density, bed uniformity and bed width-to height ratios significant process intensification can be achieved. Larger gas-solid slip velocities lead to intensification of interfacial transfer of mass, energy and momentum and to drastic reduction of the gas-to-solid space time ratio. The presented work focuses on the design, construction and demonstration of a GSVR for the fast pyrolysis of biomass. Fast pyrolysis is regarded as one of key potential technologies for the production of chemicals, fuels and energy from biomass and the GSVR can provide advantages to this process.

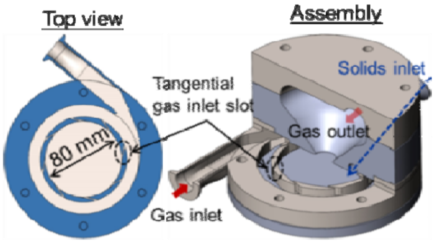

Figure 1. Gas-Solid Vortex Reactor schematics

The GSVR design consists of two concentric cylinders in which the fluidization gas is distributed around the annulus and enters the reactor chamber via eight rectangular 1 mm width inlet slots positioned at a 10° angle with respect to the tangent. The axial length of the reactor is 15 mm and the internal diameter of the reactor chamber is 80 mm. Biomass is fed into the reactor, next to the gas inlet slots, through a circular conduit of 10 mm diameter positioned at a 18° angle with respect to the horizontal plane as can be seen in Figure 1. Momentum is transferred from the gas to the particles, causing them to rotate and generating a large radially-outwards centrifugal force, which opposes the radially in-ward gas-solid drag force. Computational Fluid Dynamic simulations have shown that unreacted biomass tend to occupy the space next to the inner cylindrical wall [2]. Due to its lower size and density, char would be more expanded in the radial direction. Mass and energy balances on the GSVR showed that biomass mass flow rates from 1.4×10^{-4}-8.3×10^{-4} kg s^{-1} can be processed. The corresponding gas (N_2) mass flow rates and gas inlet temperatures are respectively 5.0×10^{-3}-1.0×10^{-2} kg s^{-1} and 800-923 K.

The operation conditions that maximize the yield of fast pyrolysis bio-oil have been established: high interfacial heat transfer, rapid removal of the pyrolysis vapors, and precise temperature control. Convective heat transfer coefficients of 300-450 $Wm^{-2}K^{-1}$, *i.e.*, three to five times those of conventional fluidized beds, can be reached in the GSVR. The estimated space time of the pyrolysis vapors before reaching the quenching section ranges from 50 to 110 ms. These space times are substantially lower than in rotating cone and fluidized bed fast pyrolysis reactors, varying from 0.5 to 2 s. The enhanced heat transfer and bed uniformity allows gaining improved control of the pyrolysis temperature. The simulations show that the temperature of the gas drops sharply after entering the reactor to a value which can be adjusted by the gas-to-biomass mass flow ratio. Biomass particles heat up almost instantaneously, until a value close to the final temperature of the gas. As a consequence of this improved temperature control and uniformity it is possible to produce bio-oils with a higher selectivity towards targeted components such as bio-aromatics.

The current demonstration unit consists of five sections: biomass feeding, gas heating, GSVR, char separation and bio-oil condensation. The biomass feeding section comprises a gravimetric feeder connected to an "*in-house*" developed injector screw. The gas heating section consists of a N_2 dewar connected in series with an electric vaporizer and two electric heating modules. Downstream of the GSVR, char is separated by means of a high throughput cyclone and a high efficiency cyclone. After leaving the reactor the pyrolysis vapors are tangentially send into a double tube heat exchanger integrated with an electrostatic precipitator. The heat exchanger is folded in a double U form, which allows collecting a carbon-rich and a water-rich oil. The fast pyrolysis process benefits in terms of yields and bio-oil quality from the advantages provided by the GSVR. The experimental set-up and results obtained with this unit will be discussed, with especial emphasis on its process intensification capabilities.

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Acknowledgements

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MODERN BIO-DERIVED FUELS OF DIESEL ENGINES

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The availability of fossil energy carriers and their expected quantity decrease, the uneven geographical distribution, the strengthening of environmental awareness, the sustainable mobility, all will require further research and development of motor fuels from alternative resources [1]. One of the most important opportunities among the possible solutions is the conversion of non-food based biomass and different wastes.

The presentation gives a brief overview of the classification of advanced alternative motor fuels suitable for diesel engines. The possible feeds meeting the previous criteria, their availability, especially the waste ones are particularly highlighted in connection of the regulatory developments of the EU.

The main objectives of the research work were to produce biofuels having similar or better quality than crude oil based distillates, they can be used in the existing logistic system, having high hydrogen content and their feedstocks are based on waste or non-food sources. Taking into account the biomass by-products and waste materials the lignocellulose materials are available in the largest quantities. In addition, an essential raw material sources include natural and waste triglycerides and fatty acids. In the presentation, the following conversion pathways are describes in detail [1-4]:

- The synthesis of bio-paraffin from lignocellulose materials through sugar molecules with their multi-step conversion.
- The production of normal- and iso-paraffin from biomass through synthesis gas and Fischer-Tropsch (FT) synthesis, with the hydrocracking and isomerisation of heavy FT waxes.
- The hydrogenation of waste triglycerides and fatty acids.
- The oxygen-free fast pyrolysis of lignocellulose at 450-600 °C, then further chemical conversion of the bio-oil, especially hydrogenation.

In the following we summarize our research results related to normal and iso-paraffin production for the last three options since the first approach contains a lot of steps, and so its economic viability is highly questionable. During the tests of the applicability of the given raw materials we used different catalytic systems chosen in a target oriented way.

Gasoil fractions were obtained with 29-34 % yield, at favourable operating conditions (350 °C, 50 bar) on catalysts found the most suitable (noble metal/AlSB-15 and composite catalyst having classified composition) from high molecular weight waxes produced from synthesis gas conversion of biomass. The iso-paraffin content of them was > 70 % (mainly mono-branched ones), the derived cetane number was > 60, the CFPP value was < -15 °C.

We concluded based on the results of the specific hydrocracking experiments of different triglycerides/fatty acid feedstocks, that bio-gasoil could be produced from high erucic acid containing rapeseed oil (non-food) with higher yield and less hydrogen consumption than the hydrogenation of edible rapeseed oil. Also favourable results were obtained with the combined transformation of high sulphur (1.2 %) and high aromatics containing (40 %) petroleum-derived distillate with waste animal fat from the waste protein processing plants.

In case of the feed containing 10 % waste animal fat on sulphided transition metal catalyst at favourable operational conditions the yield was > 95 % (theoretical value < 97 %) the cetane number of the product was ≥ 56. It is important to emphasize that the ILUC value of the waste feedstock is practically zero.

The two-step conversion of bio-oil obtained from the pyrolysis of wood is still resulted 4-5% yield of oxygen-containing product mixture with relatively modest yield (< 50 %). The product, however, was soluble in petroleum based hydrocarbons. This is very important because only a mixture could be processed efficiently (e.g. in an existing refinery plant) to obtain products of acceptable quality.

Based on the foregoing results we concluded that for current diesel engines only high-quality, high-iso-paraffin containing, environmentally friendly motor fuels based on non-food and waste triglyceride/fatty acids feedstocks could be produced economically.

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OP-III-6

PYROLYSIS FOR THE PRODUCTION OF SUGARS FROM CELLULOSE-RICH BIOMASS

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The pyrolysis of biomass has been studied extensively for more than a hundred years. Nevertheless, from recent reviews [1] it can be concluded that although progress is made in the detailed understanding, predictive models of the chemistry and transport processes (mass and energy) are lacking at molecular, cell, particle and reactor level.

For decades, fast pyrolysis has been advocated to be a promising technology for the production of a bio-based energy carrier, called bio-oil, which can replace fossil fuels in the heating and transportation sector. Yet, slow market introduction of the technology and adverse properties of the bio-oil point out the room for improvement. Optimization could be achieved via predictive reaction & transport models from which optimal process conditions, leading to the highest value of the product slate, can be obtained. With respect to the product slate it is the author's view that it is worthwhile to explore the production of feeds for fermentation (sugars) and the chemical industry (e.g. sugars, aromatics / phenols, acetic acid, glycolaldehyde) instead of, or next to, bio-oil for energy applications.

This paper aims at advancing the understanding of reactions and transport phenomenon by pyrolysing cellulose at conditions that minimize non-isothermality and maximize escape and quenching rates of products leaving the reacting particle. High escape (removal) rates of the products will reduce the extent to which they undergo reactions while still being part of the pyrolysing cellulose sample. Fast quenching minimizes reactions in the vapour phase and in the ejected fragments (aerosols). Hence, we have attempted to study the first stages and products of the pyrolysis process. To do so a screen-heater reactor has been designed that combines a high heating rate (5000 °C/s) of the reacting sample with fast removal (operation under 5 mbar) and quenching (0.02 s) of the products.

As most important result, yields of lumped component classes (gas, solid residue, condensed product), (anhydro)-sugars (DP_1 to DP_5,), and glycolaldehyde were determined as a function of the final temperature of the screens in the range of 330 °C to 765 °C. To the best of our knowledge, we have been the first to observe experimentally that it is possible to convert cellulose in the broad temperature range of 400 °C to 765 °C into hydrolysable sugars with a high and constant yield (65-70 % on carbon basis, see Figure 1) while producing only a very limited amount of lights and gas (< 1 %). Below 450 °C solid residue was found, though this turned out to be unconverted cellulose, not char. The results indicate that depolymerisation to anhydro-sugars is a true primary reaction, gas formation not and that char formation can be, as was already known, avoided. Evidence is accumulating that the distribution of the polymerization degree of the produced sugars is determined by the interplay of chemistry and heat and mass transfer at cellulose particle level (see Figure 2). A newly developed model including the aforementioned processes has turned out to provide adequate predictions of the measured trends. It has been found that light compounds and gases are formed predominantly in the vapour phase, most likely from non-sugar molecules. The heating rate of the particle, the rate with which decay products escape from the particle, and the quenching rate of these escaped products can be controlled and can thus be used to produce target products (e.g. fermentable sugar or oligo-sugars) in significant amounts from cellulose or cellulose-rich feedstocks (e.g. recycle paper). In this way, the advantages of thermochemical processes in comparison to biotech concepts, such as high conversion rates & products not being heavily diluted with water, are combined with an increased value of the product slate.

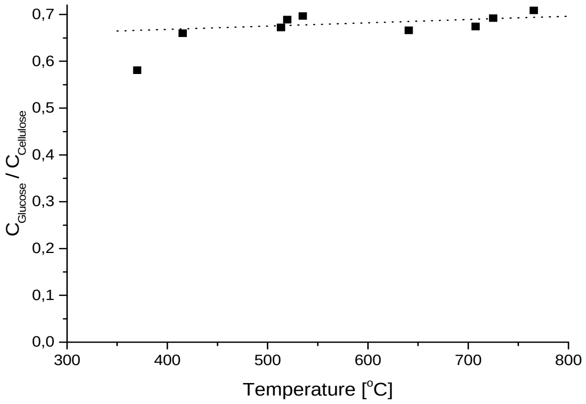

Figure 1. Sugar (total) yield as function of temperature

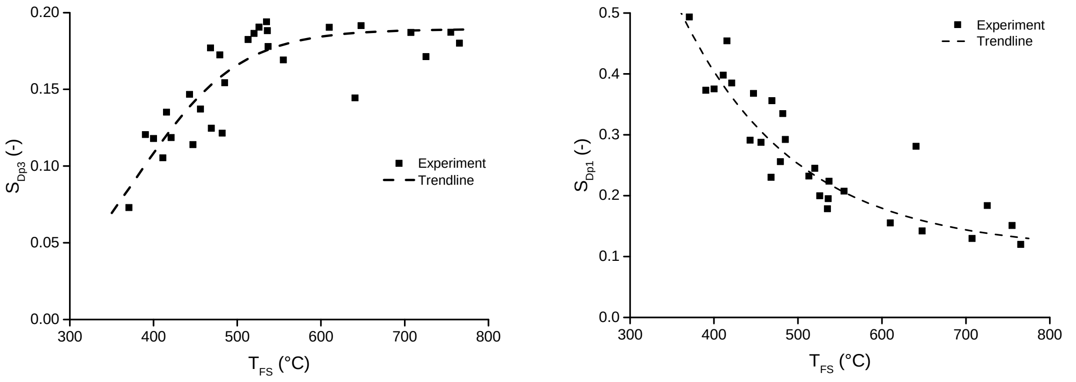

Figure 2. Selectivity of monomer (right) and trimer (left) as function of temperature

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OP-III-7

UNDERSTANDING AND DEVELOPING A NOVEL MATHEMATICAL MODEL FOR LIGHT DISTRIBUTION INSIDE THE MICROALGAE CULTURE

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Microalgal biofixation of carbon dioxide in photobioreactors recently came significantly into researchers' attention as an alternative sustainable CO_2 removal approaches. However, it has not been commercialized due to several problems while photon availability in the culture is in top of them [1, 2]. To investigate efficiency of illumination and photosynthesis process, an accurate light distribution model can be quite helpful. The most popular light model is used to simulate light absorbance in a microalgae culture is based on Beer-Lambert model which is not accurate enough especially in dense cultures [3, 4].

In this study a novel mathematical model is developed to improve Beer-Lambert model by using experimental data which can predict local light intensity inside the culture more accurately. To investigate the interior light distribution in microalgae culture, local light intensity in the culture at different incident light intensities in various biomass concentrations is measured in different geometries. Then achieved data is used for developing a mathematical modelling of light distribution by non-linear regression of experimental variables and statistical parameters were determined. The model was validated by using some other experimental data at different conditions of incident light intensity and biomass concentration (Figure 1). Meanwhile, results of new model were compared with Beer-Lambert. Afterwards, average light intensity can be calculated mathematically. Subsequently, a kinetic model can be used to predict biomass growth rate as a function of average irradiance to investigate productivity in the photobioreactor.

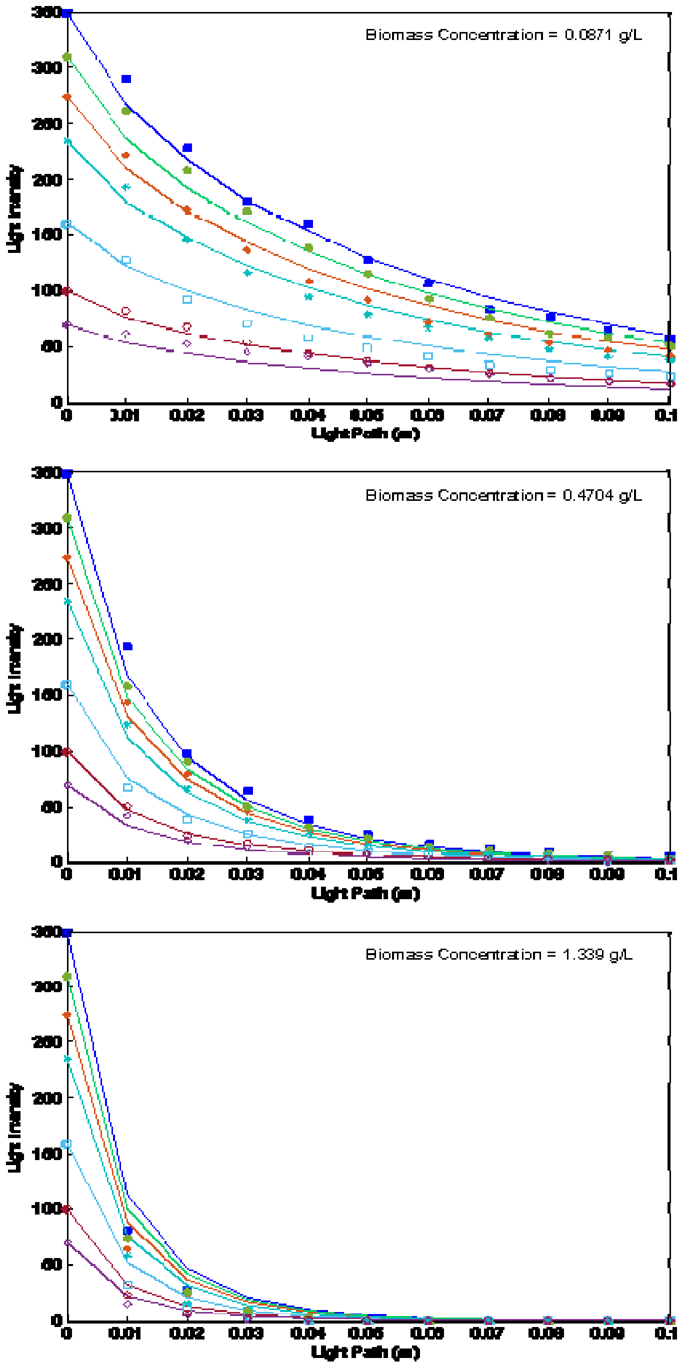

Figure 1-(a, b, c). Data and simulation results for light intensity (μmol m^{-2} s^{-1}) vs light path (m) at different biomass concentrations of 0.0871, 0.4704 and 1.339 g L^{-1}

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OP-III-8

GAS DIFFUSION ELECTROCATALYTIC REACTORS FOR CO_2 UTILISATION

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One of the main challenges of the 21st century will be satisfying the demand of energy while achieving the required carbon dioxide (CO_2) reductions to mitigate global warming. In this context, the development of technologies able to capture and convert CO_2 into useful chemicals is continuously growing. Among the different CO_2 conversion technologies, the electrochemical reduction of CO_2, using production peaks from renewable energies, appears as an innovative and feasible approach that is entering the stage of gradual implementation [1]. Hydrocarbons, such as methane (CH_4) and ethylene (C_2H_4), which could be applied in energy generation processes, can be obtained using this technology [2].

However, some aspects still limit the widespread use of this technology. Among them, the slow kinetics of CO_2 reduction and the low reaction and Faradaic efficiencies, which are directly related to the electrocatalytic material and cell configuration [3]. In this sense, gas diffusion electrodes (GDEs) have been proposed to alleviate mass transport limitations across the gas-liquid interface and to the catalyst surface [4]. This configuration may reduce mass transfer limitations and the problems associated with the low solubility of CO_2 in water. Besides, copper (Cu)-based electrocatalytic materials present both intermediate hydrogen overpotentials and carbon monoxide adsorption allowing further reduction to hydrocarbons [5].

Therefore, the purpose of this work is to evaluate the performance of a divided filter-press electrochemical cell for the continuous electroreduction of CO_2 (in gas phase) to hydrocarbons under ambient conditions when a Membrane Electrode Assembly (MEA) configuration and a Cu nanoparticle (60-80 nm)-based surface is used as working electrode. A DSA plate is selected as the anode, along with an Ag/AgCl saturated with KCl as a reference electrode. An aqueous $KHCO_3$ is used as anolyte and a cation exchange membrane (Nafion® 117) divides the cathodic and anodic compartments in the cell. A scheme of the electrocatalytic reactor is shown in Figure 1. The gaseous products are analysed on line by a MicroGC (3000 MicroGC, Inficon), quantifying the concentration of produced hydrocarbons within different operations times.

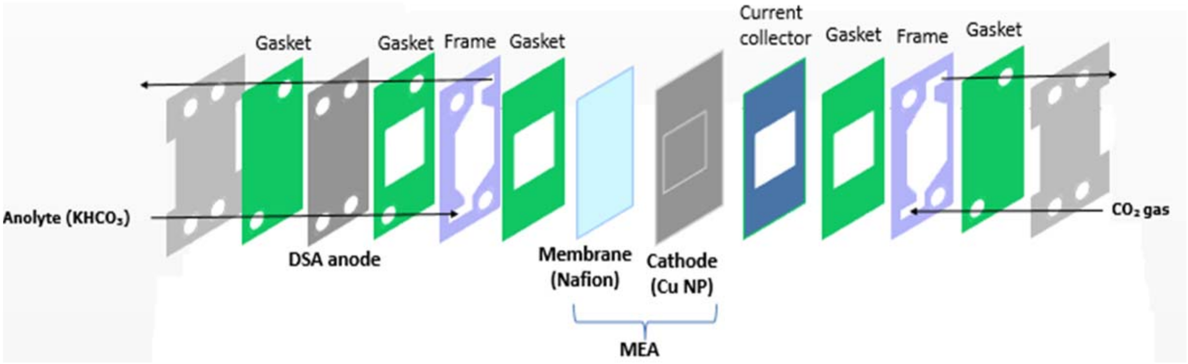

Figure 1. Scheme of the electrochemical cell

Particular emphasis is placed on evaluating and comparing the production of hydrocarbons and Faradaic efficiencies at the Cu-based GDEs (with different catalytic loadings) when different levels of cathodic voltage (-2.4 to -1.8 V vs. Ag/AgCl), feed CO_2 flow rates (Q = 150-300 mL/min), and anolyte flow rates (Q = 5-30 mL/min) are applied. Then, the reaction pathways for the reduction of CO_2 to products may be deduced, which is crucial to make this system technically viable and competitive at industrial scale.

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OP-III-9

CONTROLLED MULTIPHASE OXIDATIONS FOR CONTINUOUS MANUFACTURING OF FINE CHEMICALS

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In recent years, greater awareness of environmental and safety issues has led to increasingly stringent regulatory controls on manufacturing processes, fuelling demand for 'green' chemical technologies that can deliver greater atom, process and economic efficiency [1]. Currently, chemical technologies adopted in pharmaceutical industries are based on multi-purpose batch/semi-batch reactors used in sequential multi-step synthesis and each step requires one further unit operation for product separation. As a result, the production of fine chemicals and pharmaceuticals suffers from very poor E-factors [2] (typically 25→100) and high costs. Low space-time yields and difficulties in process control (scale-up in particular) are amongst other disadvantages of batch manufacturing processes. Another great challenge for the pharmaceutical industry is development of 'greener' oxidation methods due to the safety issues of transportation and storage of organic and inorganic peroxides [3, 4].

In order to address these issues, there is growing interest in the design and development of fully integrated continuous processes. Moreover, in a recent survey of key green engineering research areas [5] 'continuous processing' has been identified as the top priority for delivering improved cost-effectiveness, quality, safety and environmental standards to the pharmaceutical industry. In this project we aim to develop a continuous process with on-site generation of oxidants that can offer an elegant, safe, environmentally-benign, atom- and energy-efficient solution to biphasic oxidation reactions for the manufacturing of high-value chemicals.

In our integrated scalable continuous process (Figure 1) we utilize synergy between (i) continuous pulse-flow membrane emulsification for generation of emulsions with an oxidant in the aqueous phase and a reactant in the organic phase, (ii) meso-scale oscillating pulse flow reactors with periodic structure for operation of bi-phasic oxidation reactions, (iii) separation module for product extraction, and (iv) continuous electrochemical reactor for generation/regeneration of peroxodisulfate solutions [6].

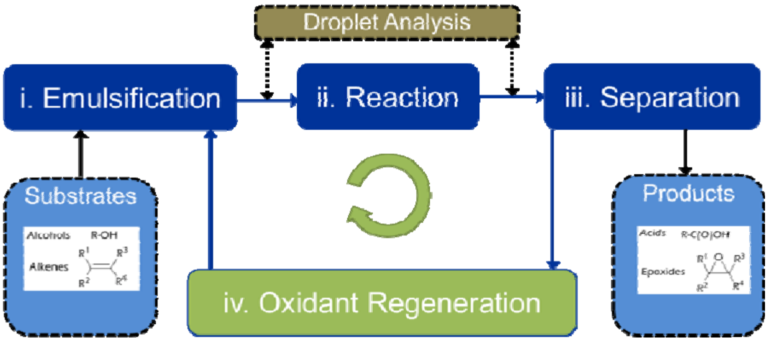

Figure 1. Scheme of the integrated continuous biphasic process

We studied in details and optimized the controllable continuous generation of unstable liquid-liquid emulsions and influence of droplet size on reaction rate using fast image capture technology and HPLC. We also investigated utilization of ammonium peroxodisulphate in batch and continuous oxidations of alcohols to acids and alkenes to 1, 2-diols, post-reaction separation in extraction unit to enable recycling of the oxidant, and regeneration of oxidant in an aqueous solution by a single-pass electrochemical reactor [5]. Finally, the applicability of the developed integrated process for oxidation of aromatic alkenes has been demonstrated.

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OP-III-10

EFFECT OF Re OR Sn ADDITION UPON CONVERSION REACTION OF ETHANOL OVER SUPPORTED Ir CATALYST AND Ru CATALYST EMPLOYING CLOSED BATCH REACTOR AND FIXED-BED FLOW REACTOR

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Recently forcus has increased on producing organic compounds from substitutive low materials anticipating the possible exhaustion of crude oil. Ethanol(EtOH) is one of the suitable candidates since it has low toxicity and can be produced from renewable biomass. C4 organic compounds such as 1-butanol(1-BuOH) and ethyl acetate(AcOEt) have wide application in industries like plasticizers and solvents. To date, these materials are mainly produced through petrochemical processes;1-BuOH is produced by hydroformylation of propylene and AcOEt by dimerization of acetaldehyde(AcH) through Wacker oxidation of ethylene. Direct formation of these useful C4 compounds from EtOH is attractive from the industrial viewpoint. In this work, we investigate Re or Sn addition effect over various supported Ir and Ru metal catalysts upon the activity and selectivity of 1-BuOH and AcOEt formations from EtOH.

Supported metal catalysts (0.5-15 wt %) were prepared by the conventional impregnation method. The Re or Sn added metal catalysts (1:1 atomic ratio) were prepared by the successive impregnation method. In the case of closed batch-reactor the catalytic reaction was carried out as follows; after H_2 reduction of 0.15 g catalysts at 523 K, a mixture of ethanol (EtOH;168 mmol) and *n*-dodecane (0.82 mmol) was charged into an autoclave under N_2 atmosphere. The reaction was carried out at 473 K (2.8 MPa) with stirring the reaction mixture. In the case of Fixed bed flow reactor, the reaction was conducted under atmospheric pressure in a fixed-bed quartz reactor (i.d. 10 mm). After H_2 reduction of the catalyst (2.0 g) (50 ml min^{-1},100 % H_2) at 673 K, the mixed gases of EtOH vapor and N_2 (1:10 vol %) flew through the catalyst bed at various contact times. Both gaseous and liquid phases were periodically sampled and analysed. The amounts of the products were determined using a GC-TCD for a gaseous phase and a GC-FID for a liquid phase, respectively.

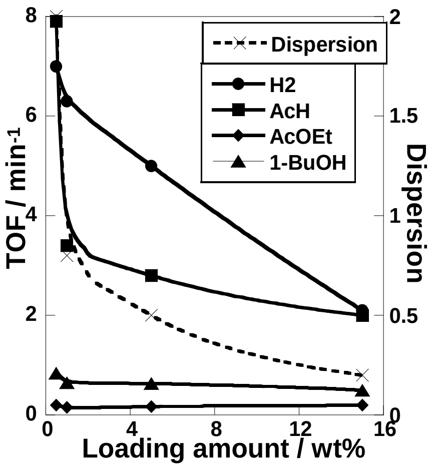

Fig. 1. Ir dispersion and TOF of the products over Ir/ZrO_2 at 473K

In order to find suitable metal candidates for EtOH condensataion to form C4 compounds, we have first compared Al_2O_3 supported Ru, Rh, Ir and Pt catalysts (5 wt %) using a closed batch-reactor at 473 K, and found that Ir/Al_2O_3 is the most active for 1-BuOH formation, whereas Ru/Al_2O_3 is the most selective among the examined catalysts. Next, we have carried out the reaction using various supported Ir catalysts to determine surtable supports for EtOH condensation. Ir/ZrO_2 also gave H_2 and 1-BuOH as main products with higher selectivity than Ir/Al_2O_3. The relations between Ir dispersion and TOF values of the rates of H_2, AcH, 1-BuOH and AcOEt formation were shown in Fig. 1. The rates of H_2 and AcH formation were well dependent on the dispersion of metal particle size, suggesting that dehydrogenation of EtOH is size-sensitive. On the other hand, the rates of 1-BuOH and AcOEt formations were less dependent on the particle size, suggesting that aldol condensation of AcH over supports is the rate determing step of 1-BuOH and AcOEt formations. Similar relations were obtained in the case of Ru/Al_2O_3.

In order to enhance the activity for C4 compound formation, Sn or Re was added to Ir/TiO_2 (5 wt %) and Ru/Al_2O_3 (5 wt %). As summarized in Table 1, AcOEt became the main product instead of 1-BuOH. Strong FT-IR bands of adsorbed pyridine were observed on these catalysts, suggesting that the Lewis acidity derived from the additives led to the dramatic change of selectivity by hemiacetal formation.

Table 1. Selectivity (%) of products and TOFs (min^{-1}) over various catalysts (5 wt %)

Catalysts (5 wt %)	Disper. (%)	Reac. temp.	**Reactor**	Selectivity (%) of products after 24h reaction						EtOH conv.%
				H_2	CH_4	CO_2	AcH	AcOEt	1-BuOH	
Ir/TiO_2	40.3	473 K	closed	39.8	2.8	4.8	15.9	4.4	32.3	17.4
Ir-Re/TiO_2	28.3	473 K	closed	39.3	5.5	6.4	3.5	40.6	4.8	31.8
Ir-Sn/TiO_2	27.8	473 K	closed	56.6	0.0	0.0	6.7	30.0	6.7	25.8
Ru/Al_2O_3	20.0	473 K	closed	15.7	30.9	9.7	22.7	4.7	16.3	22.0
Ru-Re/Al_2O_3		473 K	closed	16.5	16.5	2.4	17.9	59.0	3.5	20.9
Ru-Sn/Al_2O_3	19.4	473 K	closed	47.3	0.0	0.0	1.7	50.3	0.7	43.3
				TOF (min^{-1}) of the initial formation rates						
Ir/Al_2O_3	78.5	473 K	closed	6.71	6.71	0.96	7.71	0.07	0.81	
		573 K	flow	1.72	1.72	0.30	0.10	0.01	0.02	
Ir/ZrO_2	49.8	473 K	closed	4.84	0.41	0.38	2.81	0.17	0.83	
		573 K	flow	2.65	2.53	0.38	0.08	0.05	0.03	

Another problem for effective C4 compounds formation in the closed batch reactor may be the inhibition of formed H_2 to the formation of AcH during the dehydrogenation of EtOH. We have studied a possibility of the use of fixed-bed flow reactor for EtOH conversion to overcome this problem. However, much higher temperature (573 K) with larger amount of catalysts (2.0 g) was needed to follow the reliable rates in the case of flow system. As compared in the bottom four columns of Table 1, the main products were H_2 and CH_4 with very small amount of C4 compounds in the flow reactor.

On the other hand, we have improved our closed batch reactor by attaching a port of hydrogen permeation membrane in order to remove formed H_2 and have succeeded in the remarkable increase of the activity of C4 compounds formation.

SORPTION-CATALYTIC SYSTEM FOR ATMOSPHERIC CO_2 METHANATION

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Nowadays due to rapid depletion of fossil fuels alternative energy sources become more attractive in energy field – the part of renewable energy will rise up to 60% of all generated energy in 2035. However, there are still some unresolved problems that prevent these technologies from being economically viable. For instance, large-scale integration of wind and solar energy into the electrical grid requires a storage and distribution technology for the excess renewable electricity produced by these fluctuating sources. One of the promising and safe methods is converting renewable electricity in methane (power to gas concept) via two steps:

1. Water electrolysis: $2H_2O = 2H_2 + O_2$;
2. Sabatier process: $CO_2 + 4H_2 = CH_4 + 2H_2O$.

Renewable methane production by Sabatier process requires a sustainable source of carbon dioxide. Direct CO_2 capture from ambient air (a.k.a. “direct air capture”, DAC) offers more flexibility compared to conventional carbon capture from large point sources. Incorporation of the DAC unit with the renewable energy storage system offers an opportunity to use anthropogenic carbon dioxide as a valuable feedstock for the production of renewable methane which can be utilized in the heating market or as a fuel for transportation.

The objective of the work is to investigate the methanation process of atmospheric CO_2. For this purpose, we developed lab-scale reactor (Fig. 1) that provides desired experimental conditions: temperature up to 400 °C, controllable gas inlet, humidity control and recirculation. The reactor has compartments for catalyst and CO_2 sorbent, which allows carrying out CO_2 desorption and methanation processes simultaneously. Our work had three stages: catalysts test, CO_2 sorbent tests and atmospheric CO_2 methanation in our sorption-catalytic system.

Kinetics of Sabatier process was studied using several heterogeneous catalysts. We tested commercial nickel as well as ruthenium catalysts synthesized using activated carbon and alumina as porous supports.

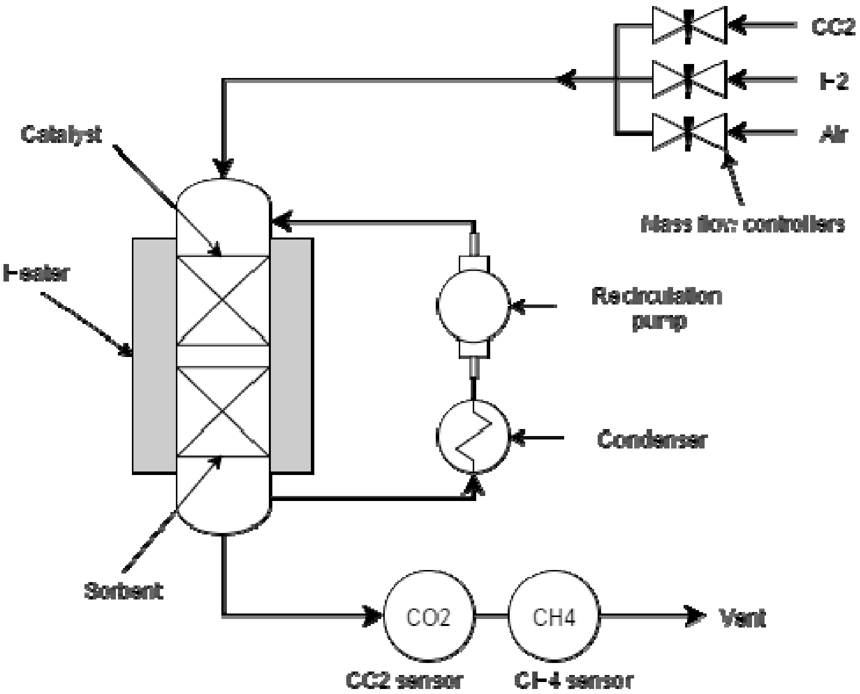

Figure 1. Scheme of the lab-scale reactor

K_2CO_3/γ-Al_2O_3 composite sorbent was synthesized as described in [1] and then tested in cycles of CO_2 sorption/desorption.

After tests catalysts and sorbent were loaded in reactor where they were investigated in sorption-catalytic process. Experiments were performed at 25 °C for sorption, and in the temperature range from 300 to 400 °C for methanation. Water was condensed by recirculation of reaction mixture through condenser. Concentrations of CO_2 and CH_4, as well as the total flow rate, were measured at the output of the reactor.

It was demonstrated that the most active methanation catalyst was Ru/Al_2O_3. Nevertheless, nickel catalyst NKM should also be considered for large-scale application due its lower price. The K_2CO_3/γ-Al_2O_3 composite sorbent showed a good stability in CO_2 sorption/desorption cycles. Sorption-catalytic system provides methanation rate of atmospheric CO_2 more than 99 % due to continuous water removing.

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OP-III-12

OPERATION STRATEGIES FOR THE SELECTIVE SYNTHESIS OF DME FROM CO_2/CO IN A MEMBRANE REACTOR

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Membrane reactors have been widely studied during the last two decades due to their high potential for the production of fuels from alternative sources. This type of reactor shows energetic and environmental advantages over conventional catalytic reactors, as a result of the increase of the reaction rate and selectivity [1].

Dimethyl Ether (DME) is an environment-friendly alternative fuel with similar characteristics to diesel fuel with a high potential in multiple markets such as transportation and power generation [2].

The incorporation of a membrane in the synthesis of DME has contributed to the elimination of H_2O from the reaction medium. Previous studies have shown that the remove of H_2O in DME synthesis promotes the reverse of Water Gas Shift Reaction (RWGS) helping the incorporation of CO_2 in the reaction [3].

In order to examine the effect of different sweep current modes and to evaluate the experimental implementation of the membrane reactor to produce DME, the permeate sweep stream has been simulated. The four types of sweeping strategies studied are: a) feed stream used in co-current mode; b) feed stream used in counter-current mode; c) H_2 stream used in co-current mode and d) H_2 stream used in counter-current mode. The simulation of the process was carried out under the following reaction conditions: Feed gas, H_2+ CO+CO_2; H_2/CO_x ratio in the feed, 3; temperature, 275 °C; pressure, 30 bar; space time, 20 $g_{cat}h\ (mol_c)^{-1}$.

Figure 1 shows the enhancement of the DME yield (ΔY_{DME}) in a membrane reactor in comparison to a fixed bed reactor, using the same catalyst and under the same reaction conditions, with CO_2/CO_x ratios between 0.25 and 1. Feed streams are represented by solid lines and H_2 streams by broken lines, coloured both blue (co-current) and green (counter-current).

The use of feed as sweep gas when comparing strategy *a* and *b* evidences that ΔY_{DME} is slightly enhanced using the second one only with CO_2/CO_x ratios ≤ 0.5, but for higher values strategy *a* shows an increase in the ΔY_{DME} of 25 % at CO_2/CO_x = 1.

In the case of H_2 to sweep the permeate, strategy *c* is similar to *a* showing a significant improvement in relation to strategy *d*. Our results shown in Figure 1 demonstrate the advantage of using a membrane reactor rather than a conventional fixed bed reactor, and this gain is higher the greater is the amount of CO_2 in the feedstock gas. Attending to the comparison between the different sweeping strategies, it can be clearly observed that using co-current mode with both streams (strategies *a* and *c*) ΔY_{DME} increases about 5%.

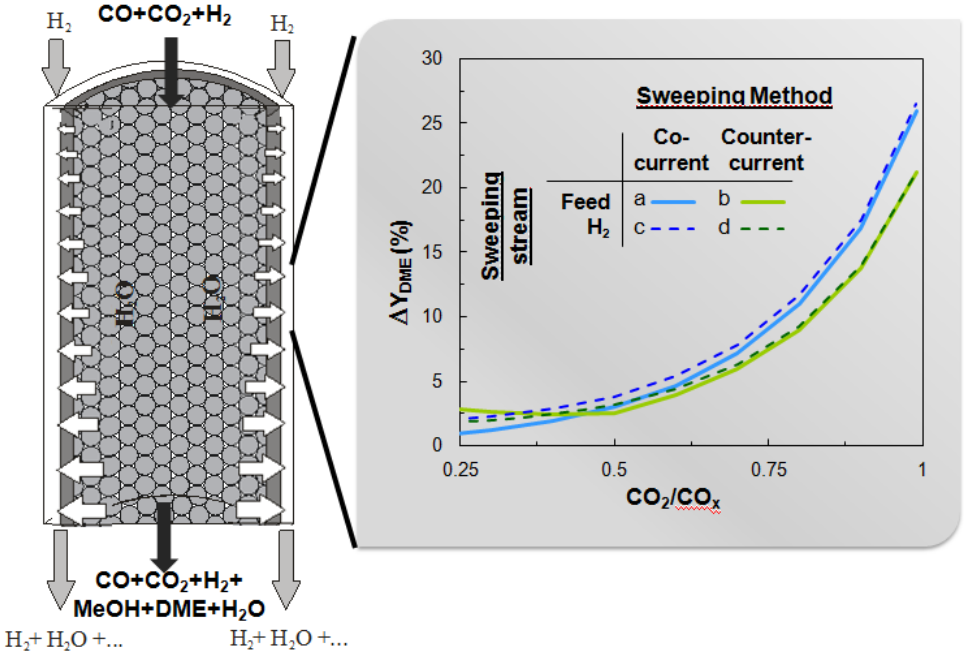

Figure 1. Reaction medium of a Membrane Reactor synthesizing DME (left). Comparison of the effect of the different sweep strategies for the enhancement of the DME yield using a membrane reactor (right)

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Acknowledgements

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OP-III-13

SIMULATION OF CARBON DIOXIDE CONVERSION TO LIQUID FUELS

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Carbon dioxide is the major greenhouse gas resulting from human activities and causes global warming and climate change [1]. Efforts are worldwide invested in reducing the accumulation of carbon dioxide in the atmosphere by reducing of the carbon dioxide emissions and simultaneously by capture and utilization of the existed carbon dioxide in the atmosphere. Additional worldwide challenge facing is the excessive consumption of crude oil in production of liquid fuels for transportation. Its reserves are limited and located in strategically problematic regions.

This current study meets these challenges; carbon dioxide utilization by conversion with hydrogen into liquid fuel was investigated by simulating a single PFR reactor as well as number of PFR reactors in series, with and without recycles. In addition, different conditions were tested: T = 300-340 °C, P = 20-30 bar, WHSV = 1-3 [h^{-1}], as well as reactants feed ratio = 2.5-3.5. The novelty in this study is in detail of different types of reactions defined. The reactions involved in this process are Reverse Water Gas Shift (RWGS), Fischer-Tropsch Synthesis (FTS), as well as oligomerization and hydrogenation of light olefins (C_2-C_4). In order to simulate the process suggested, kinetics expressions were developed based on experimental data collected, using novel Fe spinel catalyst developed [2-3]. Simulations for carbon dioxide utilized gas-to-liquids (GTL) were published [4], with the use of carbon monoxide and hydrogen as main reactants in FTS reactor. In this current study, the focus is in carbon dioxide conversion therefore only feed of carbon dioxide and hydrogen was simulated. By simulating the process, opportunities were examined to improve carbon dioxide and hydrogen conversions, improve C_{5+} hydrocarbons selectivity and reduce methane selectivity.

Simulations have shown that the carbon dioxide conversion per reactor did not reach the highest conversion defined by thermodynamic limitation, but limited by inhibition of water produced during RWGS and FTS reactions. Therefore water removal is essential in order to achieve higher conversions as proved in this study by adding reactors in series with interim separation of water and C_{5+} hydrocarbons. In addition, simulation has shown a significant contribution of light olefins oligomerization to the selectivity of C_{5+} hydrocarbons. The opportunity to introduce light olefins produced in one reactor to the next reactor or back to the same reactor via recycle stream, allowed increasing of the partial pressures and raising the oligomerization rate. Light olefins hydrogenation is also discussed in this study; its reaction rate is significantly smaller than oligomerization and is more affected by pressure.

The optimal configuration for this process is three PFR reactors in series, with recycle of 95 % of the outlet gas phase stream. The carbon dioxide and hydrogen conversions achieved are 98 % and 99 % respectively. High selectivity of C_{5+} hydrocarbons achieved and it stands at 73.7 %. The selectivity of methane is reduced to 8 %, light olefins and paraffins stands at 4 % and 4.6 % respectively and oxygenates produces as well with selectivity of 9.7 %.

The excellent results obtained by the simulation, demonstrates the ability of the suggested process to yield 630 kg of C_{5+} hydrocarbons per 1000 kg utilized carbon dioxide and 7440 kg of C_{5+} hydrocarbons per 1000 kg hydrogen. Thereby, the process and its configuration discussed in this study successfully meets the worldwide challenge of reduction of carbon dioxide in the atmosphere as well as production of alternative fuel for transportation.

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OP-III-14

THERMAL MANAGEMENT OF A SABATIER REACTOR FOR CHEMICAL FIXATION OF CO_2: SIMULATION-BASED ANALYSIS AND OPTIMIZATION

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Converting CO_2-reach streams (e.g. biogas, fermentation off-gas, flue gas) to renewable natural gas (RNG) via Sabatier reaction (CO_2 hydrogenation) is an attractive route for CO_2 utilization [1-3]. Hydrogen required for this reaction can be renewable, if produced via water electrolysis using solar and wind electricity, e.g. using highly efficient polymer electrolyte membrane (PEM) electrolyzes [4]. Other technological issues remain to be resolved, including catalyst activity and stability and heat removal (Sabatier reaction is highly exothermic) [5]. The study presented herein focuses on simulation-based optimization of the thermal management of a Sabatier reactor for CO_2 hydrogenation.

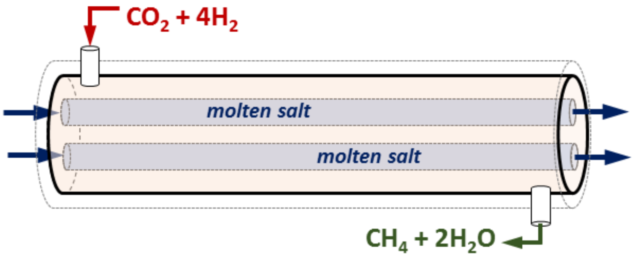
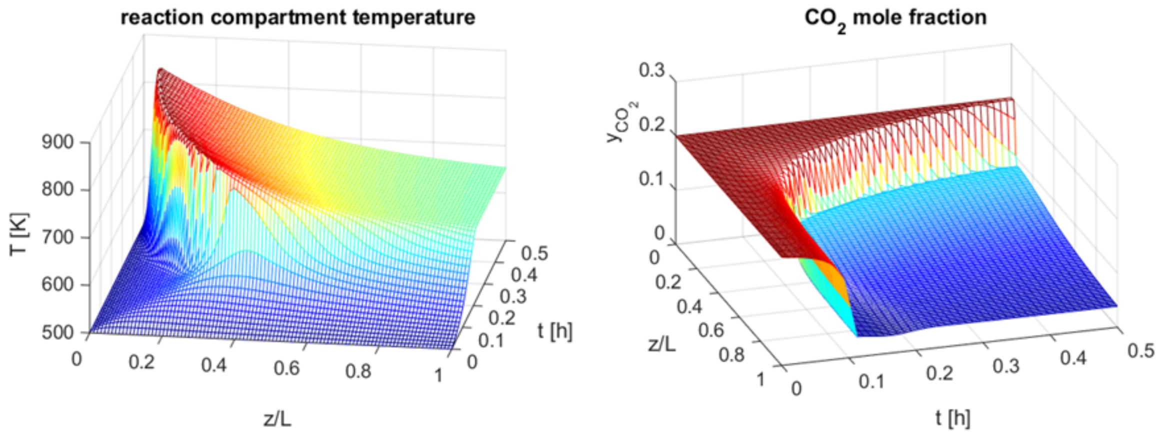


Figure 1. Heat-exchanger type packed bed Sabatier reactor

The reactor is a heat-exchanger type packed bed with a molten salt used as a coolant (**Figure 1**). Molten salts, which have excellent heat capacity and thermal conductivity, were suggested for the use as a heat transfer fluid to supply solar heat for low temperature natural gas reformers [6-9]. Herein, we suggest to use molten salts for heat removal. We use a dynamic, pseudo-homogeneous model that accounts for axial thermal dispersion [10], and temperature variations in both the reaction and coolant compartments. The main objective is to prevent the formation of a hot spot, while maximizing the reactor throughput. We search for the optimal operating conditions that favour the formation of methane but prevent exceedingly high temperatures that can lead to catalyst deactivation and molten salt decomposition.

The simulation results show that the thermal management of such a reactor is very challenging. The Sabatier reaction is highly exothermic but also reversible; the reverse reaction is highly endothermic methane reforming. Therefore, attempts to cool down the reactor can lead to complete extinction. Under certain conditions moving thermal fronts can form (**Figure 2**) and these fronts can propagate upstream or downstream. Downstream front propagation will, again, lead to eventual reactor extinction. We have identified several configurations that allow steady-state operation within the temperature regime favourable for the Sabatier reaction kinetics. Our results show that CO_2 conversions and CH_4 yields higher than 90 % are achievable due to the use of the molten salt as a highly efficient heat transfer fluid and due to the optimized thermal management.


reaction compartment temperature

CO_2 mole fraction

Figure 2. Moving fronts of temperature and concentration in the heat-exchanger type, molten salt-cooled Sabatier reactor for CO_2 conversion into renewable natural gas

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OP-III-15

AN INDUCTION HEATED REACTOR SYSTEM FOR POST-COMBUSTION CARBON CAPTURE

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Several problems with the stabilisation of electricity grid system are related to the time lag between the electricity supply and demand of the end users. Many power plants run for a limited period of time to compensate for increased electricity demand during peak hours. The amount of CO_2 generated by these power installations can be substantially reduced via the development of new demand side management strategies utilising CO_2 absorption units with a short start-up time. The sorbent can be discharged using induction heating to fill the night-time valley in electricity demand helping in the stabilisation of electricity grid [1]. Herein, a concept of RF heated fixed bed reactor [2] has been validated to remove CO_2 from a flue gas using a CaO sorbent.

The CaO sorbent was synthesised by template method with nanosized polystyrene spheres, followed by extrusion of the CaO/polystyrene mixture and calcination in an oven at 900 °C for 3 h. The reactor was made of an Inconel tube (i.d. 6 mm, 5 cm long), covered by an insulating alumina tube and positioned inside an induction coil connected to an RF-generator operated at 350 kHz (Easyheat Ambrell). The reactor was filled with the CaO sorbent (fraction: 300-600 μm). The CO_2 adsorption was performed at 650 °C from a mixture containing 30 vol % CO_2. Two desorption modes with forward or reverse flow of carrier gas relative to that in the absorption mode have been studied at 900 °C. The temperature on the surface of the Inconel tube was measured with an infrared camera (FLIR A655sc).

A very stable and reproducible operation has been observed over more than twenty absorption-desorption cycles. The application of induction heating significantly reduced the transition time required for temperature excursions between the absorption and desorption cycles. The effect of flow reversal during desorption on desorption time has been investigated. The desorption time was significantly reduced in the flow reversal mode and the total duration of a single absorption-desorption cycle was reduced by 21 %. A transient reactor model describing the reduced desorption time has been developed (Figure 1).

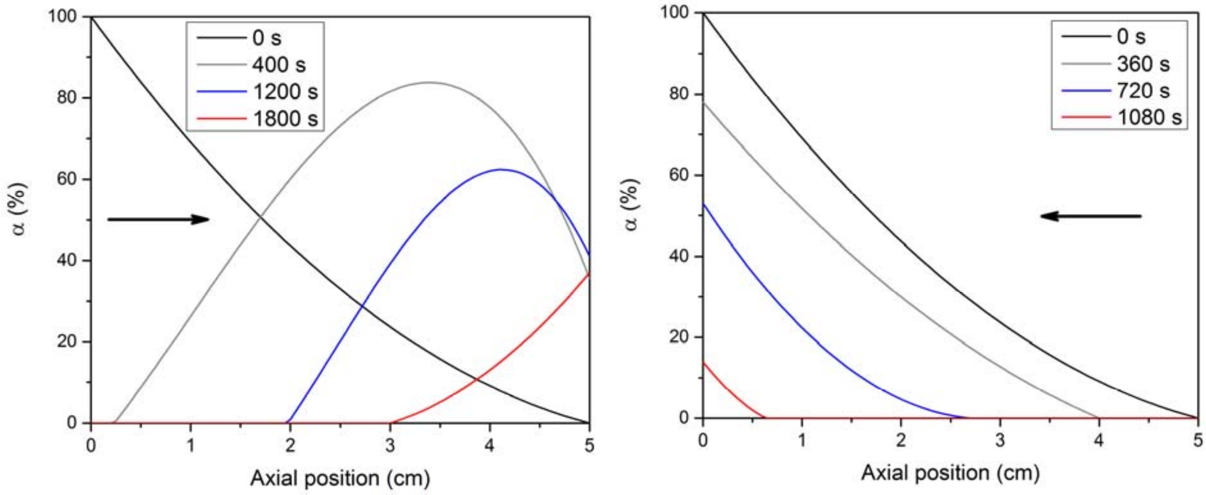

Figure 1. The $CaCO_3$ fraction (α) in the reactor as a function of axial reactor position in direct (a) and reverse (b) desorption flow mode at different reaction times. Temperature 850 °C. Purge gas flow rate: 0.12 cm^3/s

The induction heating has been proved to be an efficient alternative heating method for CO_2 capture in calcium looping cycle which provides fast heating rates and therefore short transition times between the adsorption and desorption modes which substantially reduces energy input to the system.

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Acknowledgements

The financial support provided by the European Research Council (ERC), project 279867, and Russian Science Foundation (project 15-13-20015) is gratefully acknowledged.

WET PEROXIDE OXIDATION OF PHENOL OVER BIFUNCTIONAL CARBON/ZEOLITE COMPOSITE ADSORBENT-CATALYSTS. A STUDY OF KINETICS AND DIFFUSION IN A BATCH AND FLOW REACTOR

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Catalytic wet peroxide oxidation (CWPO) is one of the most economically benign and environment friendly advanced oxidation processes. It is a promising technology for the treatment of refractory organic pollutants in industrial wastewaters. Previously we have shown that ions of Fe and Cu located in the ZSM-5 zeolites possess a high catalytic activity in the oxidative degradation of toxic organics [1-3]. Moreover, we have found a promoting effect of graphite-like carbon materials in Fenton-like processes, which are catalyzed by transition metal ions [4].

The aim of this work was to understand a role of carbon in the catalytic behavior of an adsorption-catalytic system based on (Fe and Cu)-containing ZSM-5 zeolites with supported carbon for CWPO of organics in aqueous solution as well as to study the kinetics of phenol peroxide oxidation in a batch and a flow reactors.

The bifunctional (adsorbent-catalyst) composite materials were prepared using a pyrolysis of carbon-containing compounds supported on the zeolite-containing support (H-ZSM-5 and Cu-ZSM-5) at a variation of a carbon precursor (ethylene glycol and/or polyvinyl alcohol) and conditions of the pyrolysis.

At the first step, all prepared catalysts were tested in CWPO of the phenol as model compound in a batch reactor. The best catalysts were chosen. These catalysts were prepared by pyrolysis of polyvinyl alcohol with subsequent reduction in hydrogen atmosphere in order to improve graphite-like morphology of carbon.

At the second step, the real kinetics of phenol peroxide oxidation in the batch reactor was studied over the powder composite catalyst. Reagent and catalyst concentrations and temperature were varied to design an appropriate kinetic model that describes oxidative degradation of complex organic compounds. The experiments indicated that the formation of carbon structures on the surface of Fe-and Cu-containing zeolites ZSM-5 allows us to increase their adsorptive ability and catalytic activity. A kinetic model of phenol peroxide oxidation over a carbonized zeolite catalyst was developed on the basis of the experimental data. This model describes the formation of phenol oxidation intermediates of both types, such as aromatic and acidic. It was shown that the oxidation of phenol is inhibited by phenol, hydrogen peroxide, and all the aromatic and acidic intermediates. All kinetic parameters of the model were determined.

Bifunctional composite catalysts consisting of zeolites-ceramics of two geometric shapes (trefoils and honeycomb monolith) and supported carbon were synthesized to study the real kinetics of phenol oxidation in the flow reactor. It should be noted that these forms constitute the most effective catalysts for CWPO of phenol in the case of Cu-ZSM-5 [3]. A relation between the geometric surface of the catalyst and the rate of substrate oxidation in the flow regime was studied. Trefoil catalysts having a larger geometric surface area than the honeycomb monolithic catalysts do have shown to possess a higher activity. These results again confirm an earlier assumption [3] that the catalytic activity of the extruded catalysts in CWPO of organic substrates primarily depends on the overall geometric surface rather than a porous texture. A mathematical model of the overall process on the base of the pseudo-first order simplification of the apparent kinetic rates was proposed. This model accounting for internal and external diffusion limitations over granules of various geometric shapes provides a reasonably accurate description of the experimental data in terms of phenol conversion and formation of aromatic intermediates. The suggested approach can be used for scaling up the processes of CWPO of hazardous toxicants and may be a significant advance from the laboratory scale to industrial application.

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ORAL PRESENTATIONS
Section IV.
Advanced Processing of Conventional and Unconventional Hydrocarbon Feedstocks

THE PRODUCTION OF OLEFINS BY CONJUGATED OXIDATION OF LIGHT HYDROCARBONS

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Introduction

Light olefins belong to basic chemicals. The global production of ethylene will reach 173 million tons in 2016, and that of propylene already gained 70 million tons. The constant rise of consumption of light olefins is caused mainly by the rapid increase in polyethylene and polypropylene consumption and widening the sphere of their application. But if the increasing production of ethylene can be provided by the pyrolysis of ethane, separated from natural or shale gas, the main source of propylene is the pyrolysis of more deficit and expensive heavier liquid hydrocarbons that gives predominantly again ethylene. This situation endangers by future problems with propylene and heavier olefins supply. Therefore, the development of alternative methods for production of light olefins, first of all propylene, basing on more available and inexpensive gas phase hydrocarbon stuff has important practical interest. In this study we have investigated several possible approaches to this problem that are based on the conjugated oxidation of light hydrocarbons.

Conjugated oxidative pyrolysis of propane and ethylene

Our experimental studies in two sectioned flow reactor [1] have shown the significant increase of propylene yield at the transfer from thermal to oxidative pyrolysis of propane. With the increase of temperature rapidly increases the ratio $([C_2H_4]+[C_3H_6])/([CO]+[CO_2])$. The ratio $[C_3H_6]/[C_2H_4]$ is significantly higher than that for thermal pyrolysis and even exceeds value 1 at relatively flat maximum between 620 and 660 °C, about 100 °C below than that for thermal pyrolysis. The further increase in propylene yield can be gained by conjugated oxidative pyrolysis of propane with the addition of ethylene (Fig. 1a), which can be organized so that ethylene doesn’t consume at oxidation only playing the role of catalyst. At this, noticeable formation of butene and ethylene monoxide was also observed (Fig. 1b).

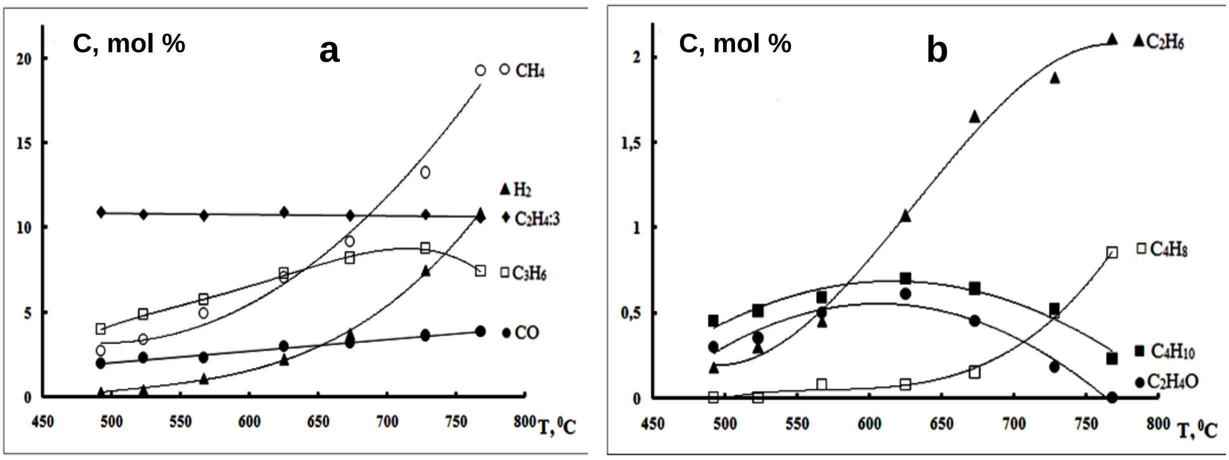

Fig. 1. Temperature dependence of concentration of products of oxidative pyrolysis of mixture C_2H_4 : C_3H_8 : O_2 = 4.5 : 8 : 1. *P* = 660 Torr, *t* = 4.5 s.

Conjugated oxidation of ethylene and methane

By the same experimental technique it was also reviled that at the oxidation of ethylene the addition of methane noticeably increases the yield of propylene [2]. It opens the possibility not only to increase, but as well to regulate the propylene/ethylene ratio at the ethane pyrolysis. Besides, if the oxidative coupling of methane (OCM) will be industrialized at last, it will be possible to produce from methane propylene as well.

The interaction of methane with products of rich methane flame

By the introduction of methane in products of rich flat flameless (surface) methane flame we have also shown the principal possibility to obtain ethylene and heavier alkanes and olefins directly from methane by non-catalytic gas phase process.

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NEW MICRO-FLUIDIZED BED REACTOR APPLICATION FOR CONVERSION OF SYNGAS TO ULTRACLEAN HYDROCARBON FUELS

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Fluidized bed reactors exhibit great advantages compared to conventional fixed bed reactors, such as a fast heat dissipation (ideal for exothermic reactions) and better mass and heat transfer. Micro-fluidized bed reactor are characterized by small amounts of bed materials, high gas velocity and low flow rate, leadind to a densification of reactor and low operation costs. It is certain that this technology opens new fields of studies and applications, such as mobile processes (production of hydrogen, Fischer-Tropsch synthesis, methanation) and applications to expensive and rare products (very small amount of powders). But micro-fluidized bed reactors suffer from difficulties in precise operation and measurement. Present study was conducted to understand the fundamental hydrodynamics of micro-fluidized bed reactor and to develop a methodology for diagnostics of fluidization conditions in the designed micro-fluidized bed reactor.

Experimental work was carried out in a glass column of 8 mm inner diameter and 55 cm total length under the conditions of room temperature and pressure with Geldart [1] group A, B and A/C powders. A porous glass filter with a thickness of 2 mm and an equivalent pore size of 40-90 μm was welded at the bottom as gas distributor. Dry air, from a compressed air network, was used as fluidizing agent. Spherical glass beads with different sizes (particle density ρ_p = 2475 Kg/m^3, diameter d_p = 12-347 μm, Group B, A and A/C by Geldart's classification) were used with an initial bed height (H_0) set as two times the column inner diameter ($H_0/D = 2$). A new diagnostic methodology for characterizing flow regimes and quality based on measurement and analysis of pressure drop fluctuation signals through the bed was developed. The system consists of a differential pressure transducer (KELLER, PD-41X) connected to a probe located above the gas distributor and a data aquisition unit (NI USB-6221). The collected points were processed with LabVIEW (2013) and Matlab (2015b) softwares. The optimum sampling frequency and time length were studied and fixed at 100 Hz and 40 s, respectively.

OP-IV-2

The analysis of time-series pressure drop fluctuation signals was carried out by calculating the standard deviation, power spectral density function by Fast Fourier Transform (FFT) and time-frequency spectrogram by short-time Fourier Transform [2] to characterize and identify the minimum fluidization velocity (U_{mf}) and minimum bubbling velocity (U_{mb}), fluidization quality and flow regimes from fixed bed to Bubbling/turbulent bed.

Results show that the variation of the standard deviation according to the velocity of gas seems to be a very powerful tool to determine U_{mf} and U_{mb}. It is noted that U_{mf} increases with the diameter of the particles, and that wall effect on U_{mf} by adding an increment increases with decreasing ratio of column diameter to particle diameter (D/d_p). Major frequencies of dominant phenomena through the bed were demonstrated by the power spectral density function, while details of the evolution of flow regimes were represented by the time-frequency spectrogram. Four flow regimes were identified: channeling, multiple-bubbling, single-bubbling, bubbling/turbulent. Channeling is observed for Group A/C particles under the condition of low gas velocity with no recognizable major frequency and very small absolute pressure drop values. Multiple-bubbling is characterized by multiple major frequencies in the range of 0-5 Hz, which normally occurs with low gas velocity for Group B particles and high gas velocity for Group A particles. Single-bubbling is given by a narrow sharp single frequency ranging from 5 to 8 Hz with increasing gas velocity for Group B particles. bubling/turbulent flow was determined by a reduction in the standard deviation and splitting of single major frequency to multiple frequencies in power spectral density function and time-frequency spectrogram. The results show a good quality of fluidization for Group B and A particles beyond 95 % and acceptable quality of 72 % for Group A/C particles.

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ON THE USE OF PHASE CHANGE MATERIALS IN LOW-TEMPERATURE FISCHER-TROPSCH (LTFT) REACTORS

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Exothermic chemical reactions with high activation energy, carried out in wall-cooled, packed bed reactors exhibit parametric sensitivity and multiple stationary states. The effect of this is the formation of hotspots leading to thermal runaway if proper heat rejection is not ensured. One such reaction is the XTL (X to liquid) Low Temperature Fischer Tropsch synthesis (200-250 °C). LTFT converts synthesis gas from various precursors such as natural/shale gas, biomass, coal, waste plastics etc. to superior liquid fuels. Temperature control is crucial to the process in order to ensure longevity of the catalyst and optimise the product distribution. Traditional proportional integral and differential (PID) controllers used for temperature control in the FT process are reliant on thermocouple sensors to detect and communicate the development of micro-sized hotspots in the the catalyst pores to the controller. They are however limited by the practicality of their size and location within the reactor.

Our work examines a novel method of using phase change materials (PCM), within a hierarchical supervisory cooling system, to intensify heat transport in such chemical reactors. Chemically encapsulated PCM, with a phase transition temperature lying between a maximum nominal operating temperature and a maximum safe operating temperature can act as a rapid-responding, distributed temperature controller. By packing the encapsulated PCM with the catalyst in a fixed bed, the PCM, an "active-inert", has the two-fold effect of: (i.) providing a temporary, isothermal sink into which the enthalpy of reaction could be dissipated (ii.) and increasing the thermal capacity of the reaction bed. The PCM thus acts as a buffer and thermal flywheel- keeping the propensity for parametric sensitivity and vacillation between multiple steady states in check. Preliminary results from a 2D pseudo-homogeneous steady state mathematical model (Figure 1) show that the PCM has the effect of evening out the temperature profile within the reactor, (at varied inlet temperatures, T_0), thereby reducing temperature spikes in the reactor by a factor of up to 10.

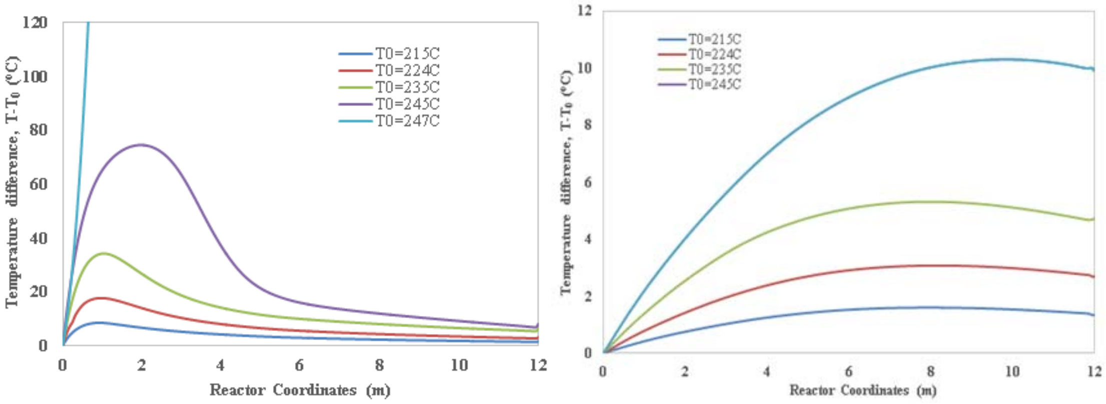

Figure 1. Temperature profiles in LTFT reactor without PCM (left) and with PCM (right) [1]

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OP-IV-4

THE EFFECT OF CATALYST PARTICLE SHAPE IN A WALL-COOLED FIXED-BED REACTOR FOR GAS-PHASE FISCHER-TROPSCH SYNTHESIS

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The Fischer-Tropsch Synthesis (FTS) is a highly exothermic polymerization reaction of syngas ($CO+H_2$) that occurs in the presence of supported Fe/Co/Ru-based catalysts to produce a wide range of paraffins, olefins and oxygenates, which is often called *syncrude*. Multi-Tubular Fixed Bed Reactors (MTFBR) and Slurry Bubble Column Reactors (SBCR) are widely employed for FTS processes [3, 6]. A MTFBR, used for gas-phase F-T synthesis, is similar to a shell and tube heat exchanger with a catalytic reaction taking place on the tube-side. A coolant, generally water, flows on the shell-side to maintain isothermal conditions in the reactor. To model such a system, detailed knowledge about shell-side interactions coupled with tube-side catalytic reaction is required. Modeling a single fixed-bed will provide information on the reactor-scale fluid-solid transport interactions that can be coupled to shell-side fluid-solid interactions.

A few reactor models for F-T synthesis have been developed in the past to analyze the performance of large-scale commercial reactors [1-4, 10]. However, all the studies were either based on a pseudo-homogeneous reactor model with traditional lumped kinetics, or a fixed-bed containing spherically-shaped catalyst particles. The use of a pseudo-homogeneous reactor model will not capture the intra-particle diffusional limitations, and for a complex reaction network with liquid products, such as the F-T synthesis, the intra-particle diffusion limitations may severely affect the performance of the reactor.

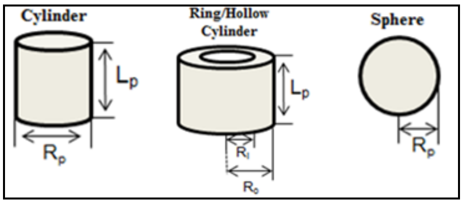

Figure 1. Catalyst shapes

In this study, a 2-D catalyst pellet model coupled with a non-isothermal 1-D heterogeneous axial dispersion reactor model was numerically simulated using COMSOL Multiphysics™ to analyze both the particle-level and reactor-level performance of three different catalyst particle shapes (sphere, cylinder, and hollow cylinder/ring; see Figure 1) for the gas-phase Fischer-Tropsch Synthesis (FTS). The Fe-based micro-kinetic olefin re-adsorption model developed by Wang *et al*. (2008) was coupled with the Soave-Redlich-Kwong (SRK) equation of state to describe the particle-scale transport-kinetic interactions and phase behavior for the gas-phase FTS [9].

The axial temperature profiles in the fixed bed are shown in Figure 2a for the three catalyst shapes. The magnitude of the hot spot is such that $(\Delta T)_{\text{Hollow Cylinder}} > (\Delta T)_{\text{Cylinder}} > (\Delta T)_{\text{Sphere}}$. The CO conversion and the reactor-scale diesel range (C_{13}-C_{17}) concentration profiles (Figure 2b & 2c) results suggest that cylinder and hollow ring shapes are preferred over spherical particle shapes, but the magnitude of the hot spot is greater for those shapes. This may lead to a higher rate of catalyst deactivation, reduce the catalyst mechanical strength, and generate unsafe reactor operating conditions. The results in the current work show the importance of understanding the axial temperature profile of a single fixed-bed in order to efficiently design a MTFBR.

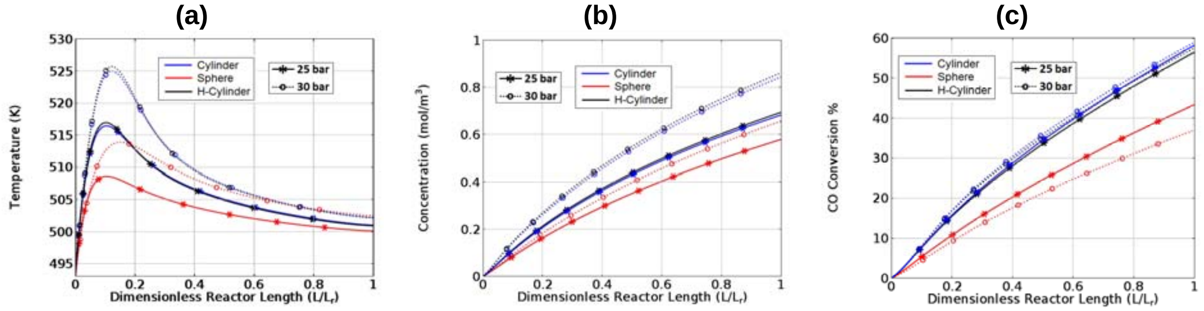

Figure 2. Axial profiles of (a) temperature, (b) CO conversion, and (c) Diesel range in the fixed-bed reactor (length L_r = 12 m, diameter D_r = 5 cm, T = 493 K, P = 25 bar & 30 bar, and H_2/CO = 2)

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CRACKING OF FUEL OIL IN THE CONTINUOUS FLOW REACTOR INITIATED BY ATMOSPHERIC OXYGEN

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At present the depth of oil refining (DOR) is a crucial parameter in these processes. It shows what part of oil is converted into useful products. In countries with highly developed oil refineries the DOR makes up over 90 % and often approaches 95-98 %. However, in Russia, the DOR is approximately 72 %. Given high prices of oil, many Russian companies are accustomed to processing large volumes of it with a low DOR and selling the rest of oil to advanced countries. However, under conditions of decreased cost of oil the problem of DOR becomes especially relevant. At present industrialized countries employ various technologies which allow raising this indicator, but they are quite costly and energy-consuming. We present a new technology which gives a possibility of low-cost modernization of installations for thermal cracking and visbreaking which provide for raising the DOR up to 90-95 %. The proposed technology makes it possible to receive from heavy oil residues additional quantities of petrol, diesel fuel and bitumen.

We have established, that in the temperature range 420-450 °C in the presence of oxygen cracking of heavy hydrocarbon feed is accelerated by increasing the rate of initiated thermal cracking chain process by radicals formed during the decomposition of peroxide compounds. Acceleration of the process is always accompanied by the formation of higher amounts of lower hydrocarbons and increases the yield of light fuel fractions.

All experiments on the thermooxidative cracking were conducted in a pilot installation with capacity of up to three liters of feed per hour over a wide range of variation thermooxidative cracking process parameters (temperature, pressure, feed rate and air). The data on thermooxidative cracking compared to traditional thermal cracking were obtained for masut, vacuum distillate and tar residue of vacuum distillation of different Russian refineries. In all cases conventional thermal processes resulted in 2-4 times less of light fuel fractions. Varying the conditions of the thermooxidative cracking always allowed bringing the quality of the heavy residue of the process to the quality parameters of commercial fuel oil or bitumen.

One of the most effective and low-cost ways of implementation of the developed process is the modernization of existing visbreaking processes by supplying a small amount of air into the soaking chamber. The results that can be achieved are shown in following table.

Table. Comparison of different processing of vacuum residue oil

PRODUCTS	The Shell VISBREAKING PROCESS	Foster VISBREAKING Wheeler/UOP PROCESS	THERMOOXIDATIVE PROCESS
	% mass	% mass	% mass
GAS	3.5	2.4	4.2
PETROL (<165 °C)	4.8	6.0	5.7
DIESEL (<350 °C)	13.6	15.5	28.7
RESIDUE (350 °C+)	79.4	76.1	61.4

Based on a large number of experimental data of the thermooxidative cracking of heavy petroleum residues of various compositions obtained over a wide variation of process parameters, several approaches to constructing the model of the process were developed.

Acknowledgements

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OP-IV-6

CHEMICAL LOOP DRY REFORMING OF METHANE: TOWARDS SHALE GAS AND BIOGAS VALORIZATION

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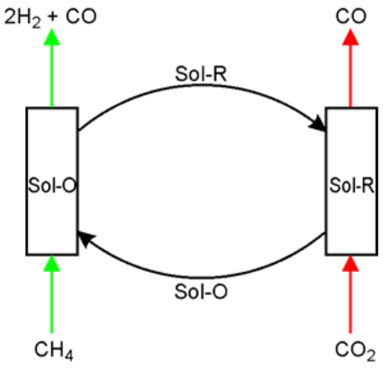
Performing methane reforming using carbon dioxide (dry reforming of methane - DRM) is an attractive solution in the context of global warming and CO_2 emissions abatement. However, DRM suffers from (i) low selectivity due, essentially, to reverse water gas shift reaction (RWGS) and (ii) catalyst deactivation by carbon deposition. This leads to low performances and low H_2/CO ratios less favorable for producing liquid fuels (Fischer-Tropsch synthesis) or of basic components for petrochemistry.

We have recently shown results [1] obtained by sequentially feeding a fixed-bed reactor with CH_4 and CO_2 in a periodic way [2,3]. The catalyst (Ni promoted CeO_2) acts as an oxygen vector. The approach is similar to chemical loop combustion or to butane-maleic anhydride reaction performed in a circulating bed reactor. Here selectivity toward oxidation of methane to syngas is sought. The catalyst and eventual coke deposits are subsequently re-oxidized by CO_2. The major advantages of this process are that (i) little or no CO_2 is present when H_2 is produced, thus limiting drastically the RWGS reaction and allowing higher selectivity and (ii) the catalyst is regenerated at each cycle thus avoiding deactivation by coking.



Recent communications concerned highly efficient Ni/CeO_2 catalyst (NGSC2016) and (Ni vs Co)/CeO_2 catalysts (ICC2016) for the treatment of pure methane. In the present communication we will present results obtained in a tentative approach towards dry reforming of more complex hydrocarbon feedstocks such as shale gas and biogas. Shale gas is characterized by a potentially high concentration of higher alkanes, in particular ethane. In such frame, we have exposed Ni/CeO_2 catalysts to dry reforming of ethane instead of methane in order to compare the reactivity of the system before considering the reforming of complex alkane mixtures.

As could be expected the contribution of carbon deposition is more important for ethane than for methane. The reoxidation of such carbon deposited is slower leading to an initial deactivation of the catalyst before reaching a stable periodic behaviour. Some ethylene is also produced during the reduction step at 800 °C.

Although these results are exploratory, they open the path for further optimization and in particular to the study of hydrocarbon mixtures.

Biogas can contain large proportions of CO_2 (20-40 %). The application of the concept of chemical loop dry reforming would mean that this CO_2 should be separated from methane in order to feed the two steps with the single components. To avoid such separation, we have studied the possibility of feeding part of the necessary CO_2 in the reductant step along with methane. Obviously feeding equivalent amounts of reactants would mean performing standard co-feed DRM.

The study has been made at 600 °C and 800°C adding 1, 2, 3 or 4 % of CO_2 to the methane feed (kept at 5 %). At 800 °C the presence of CO_2 in the CH_4 feed did not affect signicantly the performances of the system. At 600 °C, low amounts of CO_2 (1 or 2 % in 5 % methane) had no effect on the selectivity towards H_2 but considerably reduced the amount of coking. The overall conversions of CH_4 and CO_2 is also considerably increased. Above 2 % of CO_2 in CH_4 (equivalent to a 28 % CO_2-72 % CH_4 biogas composition), RWGS starts to affect the performances of the system. These results show that including ethane (for shale gas valorization) or CO_2 (for biogas) is possible in the chemical loop dry reforming of methane. In the case of biogas, this even enhances the performances of the process at low temperatures.

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Acknowledgements

The University of Lille 1 is acknowledged for providing financial support for this work as well as the Federation Chevreul.

Experimental

The catalytic test was conducted under atmospheric pressure in a fixed-bed quartz reactor. The gas stream of CH_4 or C_2H_6 (5 % in inert) named reductant step and CO_2 (5 % in inert) named oxidant step was fed to the reactor (F_T = 100 mL/min). In the case of biogas approach, the overall stoichiometric molar ratio CH_4/CO_2 was maintained at 1/1 while feeding CO_2 partly in the reductant step and the complement in the oxidant step. The outlet gases were analyzed online by a mass spectrometer. The conversion of each reactant is integrated on a full cycle. A typical cycle includes 1 min. reductant step and 1min. oxidant step for CH_4 reforming or 2 min. oxidant step for C_2H_6 reforming.

METHANOL TO GASOLINE TRANSFORMATION STUDY IN ONE AND TWO STEPS REACTOR SET UP

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The formation of various types of hydrocarbons from methanol has been studied since the end of 19th century. The earliest report of hydrocarbon formation from methanol is that of LeBel and Greene [1]. Hexamethylbenzene and light gases were identified as the main products. A new age of methanol to gasoline synthesis began with the application of various zeolites. Now the methanol to gasoline synthesis is mainly provided over a zeolite-based catalyst to light olefins (MTG) and liquid hydrocarbons typically take place in the temperature range of 300-400 °C [2]. H-ZSM-5 zeolite can be considered as the most commonly applied catalyst in this process. However process can be provided via different technological schemes and reactors.

Here we report investigation of methanol transformation to hydrocarbons using one and two reactor scheme. One reactor scheme contains only one catalyst for methanol to hydrocarbons transformation. And two reactor scheme contain one reactor for methanol to DME transformation and the other reactor for DME to hydrocarbons transformation.

Methanol to gasoline synthesis was carried out in continuous mode using one and two active reactor scheme. The laboratory set-up is presented in Fig. 1. Before the experiment the system is purged with nitrogen for 40 minutes, and then reactors are heated to needed temperature. After stabilization of reaction temperature high pressure methanol pump purge system with methanol and reaction starts. Then the exact composition of the reaction gas and liquid mixture was determined using gas chromatography (GC). In a typical two step experiment, 10 g of the catalyst of methanol to DME (γ-Al_2O_3) and DME to hydrocarbons (H-ZSM-5) synthesis is sieved and fraction of 0.125 mm was taken for reactor filling. The reactor was placed on shaker and was field by catalyst partially. The nitrogen feed rate was maintained at 10 ml/min, methanol feed rate was maintained at 0.1 ml/min. Typical reaction conditions was 350 °C for all reactors and 5 bar overall pressure. In order to analyze the composition (hydrocarbons, methanol, DME, CO, CO_2, H_2, N_2), the state of-the-art analytic complex including gas chromatographs (Crystall 2000, Russia) equipped with flame-ionization detector and catarometer was used. For determination of exact products structures composition mass spectrometer QP2010 (Shimadzu, Japan) was used.

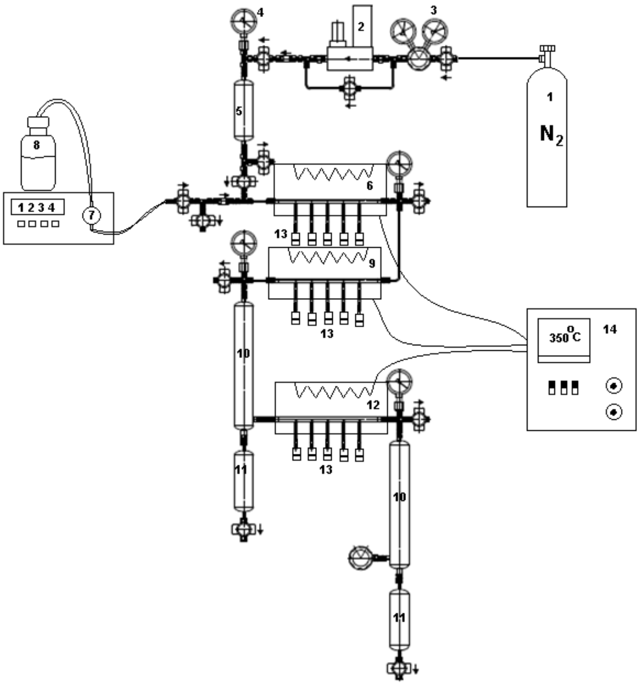

Fig. 1. The scheme of laboratory set-up of methanol to gasoline synthesis process:

1 – nitrogen tanks,
2 – nitrogen flow controller,
3 – pressure regulator,
4 – manometer,
5 – gas tank,
6 – gas mixer,
7 – high pressure pump for methanol,
8 – methanol flask,
9 – reactor for methanol to DME synthesis (in case of two reactors process)/reactor for methanol to hydrocarbons synthesis (in case of one reactor synthesis),
10 – reflux,
11 – water and methanol collector,
12 – reactor for hydrocarbons from methanol synthesis,
13 – thermocouple,
14 – thermo controller

The influence of reaction temperature and pressure were investigated in methanol to hydrocarbons transformation process. The highest methanol transformation rate for both schemes are presented in table 1.

Table 1 – The H-ZSM-5 physicochemical characteristics and methanol o hydrocarbons transformation rate for different reactor schemes

Catalyst	Si/Al[a]	C_{acid}[b], mm/g	S^c_{meso}, m^2/g	S^c_{micro}, m^2/g	W_{trans}(MeOH)[d], g(Met)/(g(Cat)*h)	
					1-reactor	2-reactors
H-ZSM-5	57	0.41	154	170	1.4	8

a – according to XPS analysis;
b – according to ammonia chemisorption;
c – according to liquid nitrogen physisorption;
d – methanol to hydrocarbons transformation rate.

The two reactor scheme therefor is more attractive in technology point of view.

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PHENOL DEOXYGENATION IN A THREE PHASE MINI SCALE REACTOR

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Bio-oils are considered as an alternative to petroleum-based sources for the production of a wide range of fuels and high value-added chemicals. The major organic compounds of the bio-oils are acids, alcohols, ethers, ketones, aldehydes, phenols, esters, sugars, furans, and nitrogen compounds. Phenols are considered as the most difficult to deoxygenate compounds and phenol is used as a representative model compound to study HDO process [1]. A range of heterogeneous materials have been tested as catalysts including nickel catalysts [2,3,4] and cobalt [4,5] catalysts. The main objective of this work is the study of the kinetics of phenol hydrodeoxygenation in a three phase mini scale reactor and the comparison of the performance of two conventional catalysts. The experiments were conducted over a NiMo/γ-Al_2O_3 and a CoMo/γ-Al_2O_3 catalyst in crushed form, in order to eliminate the internal diffusion phenomena.

The experiments were conducted in a mini scale spiral string bed reactor which was loaded with 0.25 gr of catalyst. The liquid feed consisted of 1 % wt phenol diluted in high purity organic solvent. N-dodecane and n-hexane were tested as organic solvent. The liquid feed flow rates varied within the range 2.8-8 $gr \cdot h^{-1}$. High gas flow rates were tested corresponding to G/L ratios higher than 400 Nl/l. The experiments were performed at pressures 20-40 bar, and temperatures 130-230 °C. Standard experiments were repeated for the determination of the catalyst deactivation.

The main products detected from the phenol deoxygenation catalyst at the conditions tested are cyclohexanol and cyclohexane. Small amounts of cyclohexene and traces of benzene were also detected. For the NiMo γ-Al_2O_3 catalyst cyclohexanol is the main product at high liquid feed flow rates, and its selectivity decreases with temperature increase and liquid flow rate decrease. For the CoMo/γ-Al_2O_3 catalyst the main product is cyclohexane. The differences of the performance of the two catalysts will be presented.

Benzene and cyclohexanol hydrotreatment experiments were also performed at the same conditions in order to clarify the reaction scheme and pathways for the phenol hydrodeoxygenation. The kinetic model developed fits satisfactory to the experimental data.

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THE USE OF MAGNETIC BIOCATALYST FOR OXIDATION OF PHENOL DERIVATIVES

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The oxidation of aromatic compounds is an important chemical process of fine organic synthesis. It should be noted that the oxidation processes are characterized by the formation of whole variety of by-products along with the target products. In this connection, the increase of the selectivity of oxidation processes is a priority of modern chemistry. One of the possible solutions for the above problem is the use of various enzymatic systems capable of catalyzing the oxidation processes. However, the use of enzymes in organic synthesis is faced with a number of unresolved issues related to ensuring their stability and the possibility of separation from the substrate. The solution of this problem is the immobilization of enzymes on different carriers [1,2].

Magnetic nanoparticles are a promising carrier for enzymes [3]. Immobilization of enzymes on magnetic nanoparticles allows quickly and easily separating the biocatalyst from the reaction mixture. In this paper, we propose to immobilize of peroxidase horseradish (HRP) on magnetic nanoparticles. The resulting biocatalyst can be successfully applied to the oxidation of 2,3,6-trimethylphenol by hydrogen peroxide. A result of enzymatic oxidation is obtaining of 2,3,5-trimethylhydroquinone, which is the intermediate product of vitamin E.

The synthesized biocatalyst was investigated using physico-chemical characteristics: transmission electron microscopy, FTIR spectroscopy, the study of the magnetic characteristics using a vibrating magntitometra, X-ray photoelectron spectroscopy and low-temperature nitrogen physisorption.

To obtain the magnetic nanoparticles a polyol method was used. Ethylene glycol was used as the solvent. As a result, clusters were obtained with an average diameter of 111 ± 5 nm in the form of nearly spherical, consisting of a plurality of small nanoparticles (Fig. 1).

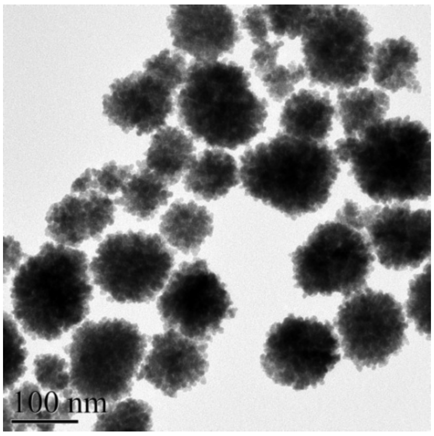

Figure 1 – The micrographs of the synthesized nanoparticles

Nanoparticles were treated with 3-aminopropyltriethoxysilane (2 μL/mL) to modify the magnetic particles by reactive amino groups. Then HRP was applied on the modified carrier.

When testing in the oxidation reaction of the biocatalyst 2,3,6-trimethylphenol an optimal conditions (the initial substrate concentration, temperature, pH) were selected.

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OP-IV-10

Bi-FUNCTIONAL SOLID PARTICLES FOR SORPTION ENHANCED STEAM METHANE REFORMING: MODELLING AND EXPERIMENTAL DATA

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The Sorption Enhanced Steam Methane Reforming (SE-SMR) process allows to convert CH_4 (e.g. from natural gas) to H_2-enriched syngas by an endothermic, catalytic steam reforming process with simultaneous CO_2 separation in situ by an exothermic, solid-sorption reaction (600-700 °C). Nickel is largely adopted as catalyst for SMR. In high-temperature conditions, CO_2 sorption is proposed to be performed by CaO conversion to $CaCO_3$ (i.e. carbonation), followed by thermal decomposition of $CaCO_3$ to renewed CaO at 800-900 °C (i.e. calcination). Iteration of carbonation-calcination cycles is the key of a continuos SE-SMR process. Natural sorbents (e.g. cacined limestone or dolomite) suffer a significant decay in sorption capacity after a few carbonation-calcination repetitions, while synthetic materials can be conceived with an inert binder matrix, to stabilize sorption capacity. Recently, it has been proposed to combine the sorption and catalytic functions in an unique porous particle [1], to reduce diffusion resistances encountered when catalyst and solo-sorbent particles are simply mixed in a reactor [2]. This work utilizes a previously developed bi-functional particle model to compare experimental data to numerical predictions about SE-SMR. Model main features are:

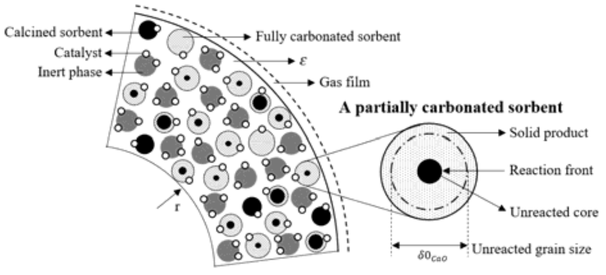

Figure 1: Schematic view of a modeled bi-functional particle

- Particle constituted by spherical grains of CaO or an inert phase, with nickel finely dispersed on grain surface and avalaible to gaseous reactants during the whole reforming process. Because of carbonation, the volume of each sorbent grain increases with a corresponding reduction of particle porosity (Figure 1).
- Local carbonation reaction rate described as first order law in CO_2 concentration and available active surface, with kinetic constant taken from literature [3].

- Catalytic activity quantified by Numaguchi and Kikuchi kinetic laws for SMR and Water Gas Shift [4].
- CaO conversion expressed as a function of diffusion of CO_2 through the carbonate layer formed around each calcium oxide grain [5].

Model simulation results were successfully compared with experimental data from:

- dynamic carbonation tests in TGA, contacting a N_2/CO_2 gas mixture with calcined dolomite particles of different size, as well as with synthetic sorbents (CaO supported on mayenite, which is an inert calcium alluminate) and synthetic bi-functional particles (CaO+Nickel on mayenite); in this latter case, the ability of the sorption model was shown to describe faithfully the influence of temperature, carbon dioxide concentration in the gas phase and number of solid carbonation cycles;
- methane steam reformig catalytic tests in a micro-reactor with a packed bed of synthetic catalyst particles (Nickel on mayenite).

All synthetic materials utilized in these tests were purposely prepared and characterized by XRD, TPR, BET-BJH method, SEM. The major goal is to verify the ability of the grain model to offer a quantitative interpretation of the carbonation phenomenon as a function of time, when powder samples are exposed to a gaseous mixture including carbon dioxide, and a plausible description of the effect of process variables on the SE-SMR. A relevant part of this study is about the influence of steam in high temperature cyclical calcination, carried out by comparing the behaviour of samples of the same material during calcination in a steam atmosphere or in an inert one, respectively. It is well known that in these cases steam is causing a reduction of the active surface and therefore of carbonation rate and final CO_2 capture capacity. The model parameter that may take into account this phenomenon is the size of calcium oxide grains, by considering its progressive increase with the number of carbonation-calcination cycles.

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ENHANCEMENT OF THE ACETYLENE YIELD FROM METHANE BY PARTIALLY DECOUPLING THE OXIDATION AND PYROLYSIS REACTIONS

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The partial oxidation (POX) of methane is the main approach to produce acetylene [1]. The reaction pathway analysis indicates that the exothermal oxidation reactions and the endothermic pyrolysis reactions are highly coupled in the POX process and thus the maximum yield of acetylene is limited to 33 %. This value cannot be further enhanced by optimizing the operating parameters [2]. A new process called partially decoupled method has been proposed and verified in this work. This process physically decoupled the oxidation and pyrolysis reactions. This method prevents methane from directly contacting with the strongly oxidizing groups and thus weakens the CO formation pathway (see Figure 1). The theoretical calculations based on the assumption of instantaneous and inert mixing of the heat carrier gas and methane shows that the maximum yield of acetylene can be enhanced to 52 %.

A jet-in-cross-flow (JICF) reactor is designed to realize this new process. This type of reactor has been successfully applied in the production of ethylene [3]. Computational fluid dynamics (CFD) simulations coupled with detailed chemical mechanism are used to investigate the influence of turbulent flow and turbulence-chemistry interaction. A modified GRI 3.0 mechanism [2], which has been verified by experimental data, is used in the simulations. The CFD model coupled with modified GRI 3.0 has been verified by simulating the original POX process. Figure 2 shows that the maximum acetylene yield of the new process can reach 42 %, which is much higher than that of the original POX process. The influence of the reactor structure parameters and operating parameters have also been investigated. The optimum nozzle number is 8 and the maximum acetylene yield decreases with the increase of diameter of the reactors. The optimum mixing ratio is 1750 K.

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OP-IV-11

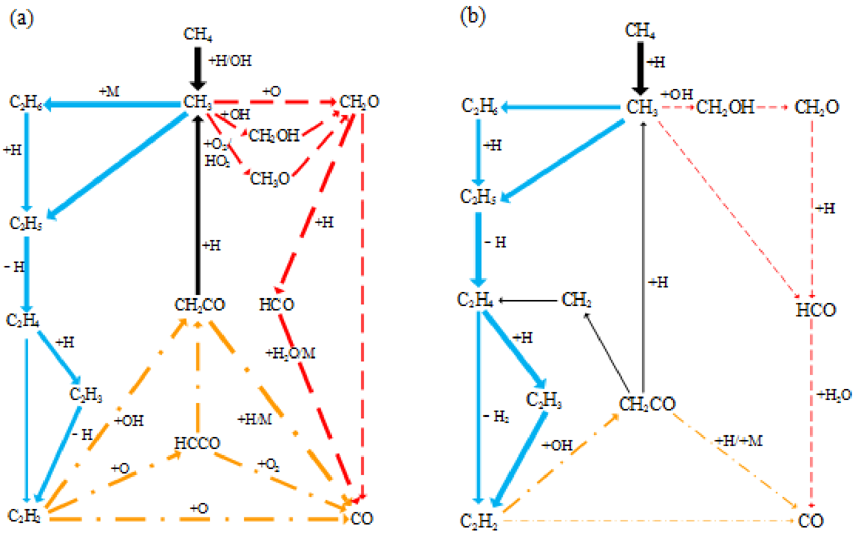

Figure 1. Simplified reaction pathways of acetylene and CO formation for (a) the original POX process before oxygen is exhausted and (b) the partially decoupled process

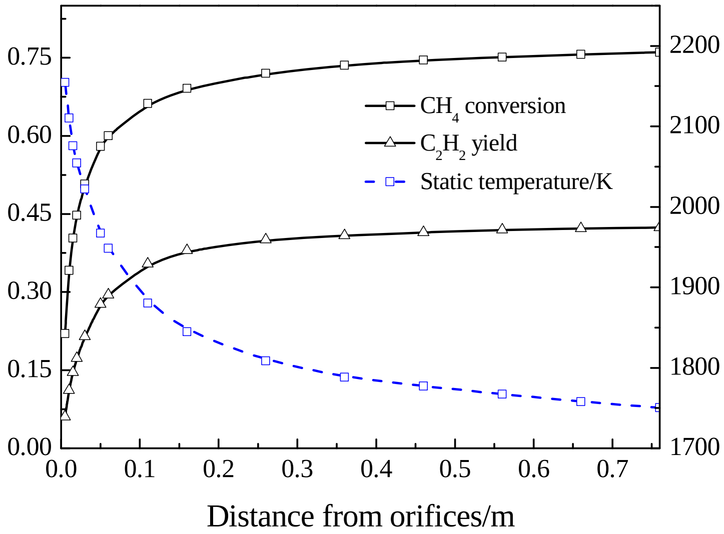

Figure 2. Simulated axial profiles of the mass-averaged static temperature, CH_4 conversion and C_2H_2 along the centerline of the partially decoupled process

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OP-IV-12

COMPUTATIONAL FLUID DYNAMICS DESIGN OF STEAM CRACKING REACTORS: EXTRUSION METHOD FOR SIMULATION OF DYNAMIC COKE LAYER GROWTH

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Steam cracking of hydrocarbons is the predominant commercial process for producing many platform chemicals such as light olefins (i.e. ethene, propene, and butadiene) and aromatics (i.e. benzene, toluene, and xylenes). A major factor for the process efficiency is the formation of a coke layer on the inner surface of the tubular shaped reactors. Due to this insulating carbonaceous layer, heat transfer to the process gas is hampered, leading to excessively high tube metal temperatures. Additionally, the cross sectional area for flow is reduced and the reactor pressure drop increases, resulting in a loss of olefin selectivity. Decoking of industrial reactors is thus inevitable. In consideration of this energetic and economic drawback, many efforts have been made towards the development of technologies to reduce coke formation. Three-dimensional coil geometries are often introduced to enhance radial mixing resulting in lower coking rates and longer run lengths.

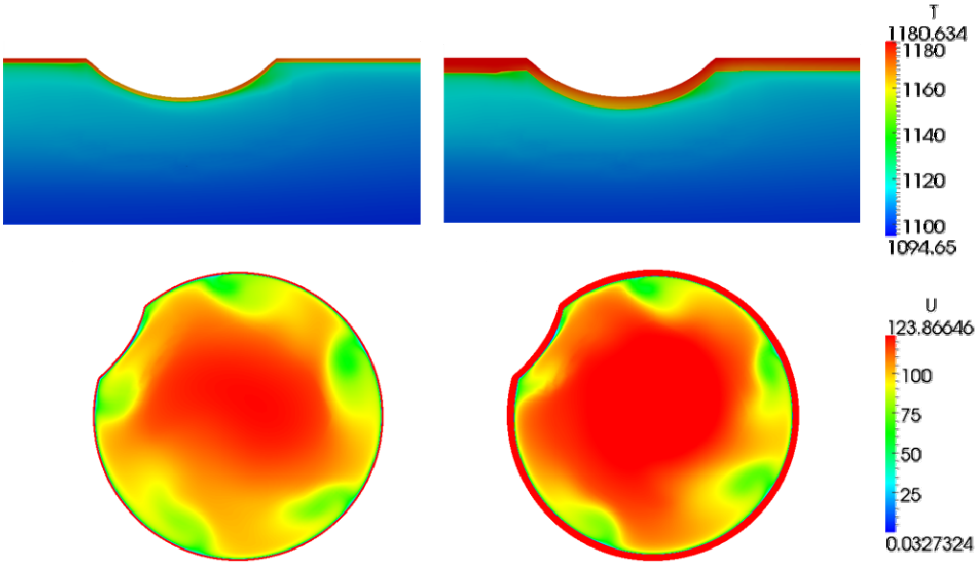

Figure 1. Coke layer growth in a slit-MERT 3D reactor geometry. The temperature profile and the velocity profile in a cross section of the reactor are shown for start-of-run conditions (left) and after 5 days of coke layer growth (right)

Our group has successfully applied computational fluid dynamics (CFD) for the evaluation of the effect of 3D reactor geometries on pressure drop, coking rates and product yields [1, 2]. These studies however focused on start-of-run performance, whereas the most attractive characteristic of the enhanced reactor designs is the extension of the run length. Determining the full economic potential of a coil hence involves tracking its performance throughout the run, i.e. as function of the time on stream. In the case of enhanced tubular geometries or reactors with a strongly non-uniform heat flux profile (e.g. due to shadow effects), the growth of the coke layer will generally not be uniform. Because of this, the reactor geometry will change in time, which will in turn influence the fluid dynamics, product yields and successive coke formation. To take this into account, the coke layer growth needs to be incorporated in the CFD simulations. An algorithm based on dynamic meshing was therefore developed for simulating coke formation on the 3D reactor geometry and tracking the geometry deformation caused by the growing coke layer. In this algorithm, the reactor mesh is updated on a regular basis as coke deposits on the reactor wall until an end-of-run constraint is met, indicating that decoking is required.

The open source CFD package OpenFOAM has been extended with a module for dynamically simulating the growing coke layer. The module includes a new library of extrusion models which makes it possible to automatically generate structured meshes of high quality on several complex 3D reactor geometries, see Figure 2. The module can be used in a post-processing step to simulate the growth of the coke layer based on the temperature and species concentrations at the gas-cokes interface.

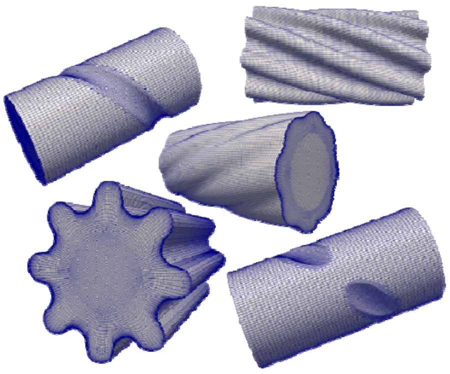

Figure 2. Structured meshes of complex 3D reactor geometries

As a proof-of-concept, a Millisecond propane cracker was simulated over the first days of its run length for a bare, a classically applied finned tube and a MERT reactor design.

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Acknowledgements

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MATHEMATICAL MODELLING OF “REACTOR – STABILIZATION COLUMN” SYSTEM IN CATALYTIC DEWAXING OF DIESEL OIL CUTS AND ATMOSPHERIC GASOIL

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The production of low freezing diesel fuel components by catalytic dewaxing of middle oil distillates (straight run diesel oil cuts and atmospheric gasoil) represents complex multi-stage system, which consist of reaction stage, stabilization of product, rectification. All stages of production are interconnected. In particular, the composition of product after dewaxing reactor influences the operation of stabilization column. This column is meant for removal of light hydrocarbons and hydrogen sulphide from the product of reactor, which is unstable hydrogenate. However, the current mode of column operation does not provide complete removal of hydrogen sulphide. As a result stable hydrogenate contains significant amount of of hydrogen sulphide. When entering into the rectification column hydrogen sulphide entirely concentrates in the overhead product (stable naphtha) and causes corrosion of overhead parts of equipment and pipes so that this decreases the operation time of the column. The aims of the current work is modelling and optimization of joint operation of dewaxing reactor and stabilization column taking into account their interconnection.

Using the developed models the influence of flow rate of overflash into the column on the content of hydrogen sulphide in stable hydrogenate at the content of hydrogen sulphide in unstable hydrogenate equal to 300, 500, 700 g was studied (Fig. 1).

As it can be seen on Fig. 1 the increasing in flow rate of overflash into stabilization column by 30 m^3/h leads to decreasing in the content of hydrogen sulphide in stable hydrogenate by 205 g. In spite of this, the content of hydrogen sulphide in stable hydrogenate is high.

The recycling of stable naphtha from rectification into the bottom of the column intensifies mass-transfer in the column and provides decreasing in the content of hydrogen sulphide in stable hydrogennate (Fig. 2).

As it can be seen on Fig. 2 the increasing in the stable naphtha flow rate into the bottom of the column by 20 m^3/h provides decreasing in the content of hydrogen sulphide in stable hydrogenate by 66 g. Nevertheless, stable hydrogenate contain hydrogen sulphide.

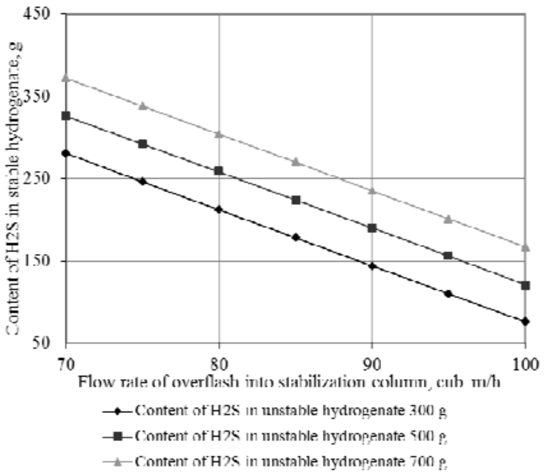

Fig. 1. The influence of overflash flow rate on the content of hydrogen sulphide in stable hydrogenate

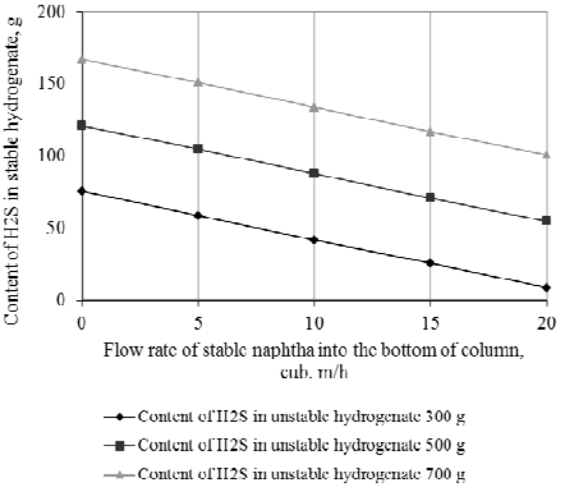

Fig. 2. The influence of stable naphtha flow rate on the content of hydrogen sulphide in stable hydrogenate

To solve this problem the hydrogen containing gas can be injected into the column. This will provide rising in the amount of light gaseous components and consequently the vapor flow up the stabilization column, which will carry more hydrogen sulphide (Fig. 3).

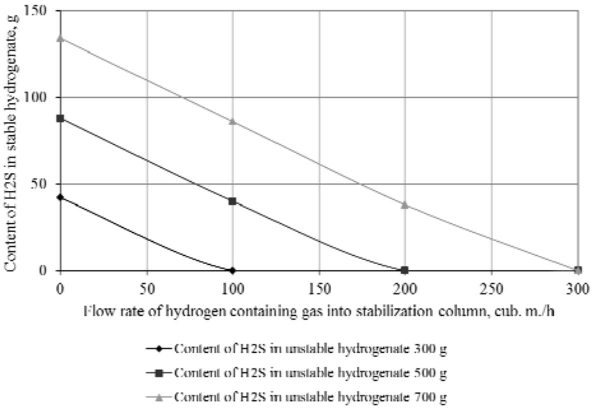

Fig. 3. The influence of hydrogen containing gas flow rate on the content of hydrogen sulphide in stable hydrogenate

Fig. 3 shows that injection of 100, 200, and 300 m^3/h of hydrogen containing gas in the column for different hydrogen sulphide contents in unstable hydrogenate equal to 300, 500, 700 g. accordingly ensures the absence of hydrogen sulphide in stable hydrogenate.

The application of developed model allows determining the optimum contitions of the column operation depending on the content of hydrogen sulphide in the product of dewaxing reactor. This ensures obtaining stable hydrogenate without hydrogen sulphide and prolongation of service life of the column.

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LOOP REACTOR MODELING FOR LUBRICANTS SYNTHESIS

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The biolubricants based on esters, in the last years have generated a great interest in the scientific community and represent an alternative to the petrochemical lubricants. Their properties are similar to those of the petrochemical lubricants but at the same time they are more degradable, less toxic and so less polluting with respect to mineral lubricants.

Typical catalysts used for the esterification reaction are acid homogeneous catalysts such as p-toluen-sulphonic acid, phosphoric acid, sulphuric acid [1]. However the use of acid homogeneous catalyst has problems derived from the necessity of product purification. On the contrary, the use of classical heterogeneous catalysts, such as the acid resins, is limited by the fact that they are not stable at temperature higher than 120 °C [2]. For esters synthesis the temperature, instead, must be higher than 180 °C to favour the elimination of water from reaction environment because the reaction is limited by chemical equilibrium. In this work we study the biolubricants synthesis, obtained by esterification reaction between fatty acid and several polyols using H_2WO_4/SiO_2 as acid catalyst.

In particular two polyol esters have been prepared by the esterification of different polyalcohols with saturated monocarboxylic acids having carbon atoms number between C9 and C18. In the present work we have studied two reactant systems: pentaerythritol (PE) and nonanoic acid, 1,3-propanediol and oleic acid.

The chosen reactor configuration was that of fixed bed recyrculated in a loop reported in the following figure (Fig. 1) where it is possible to note different units: reservoir tank (1), magnetically stirrer (2), thermocouples (3), recycle pump (4), flow meter (5), N2 line-in (6), N2 line-out (7), tubular packed bed reactor (8) and heating devices (9).

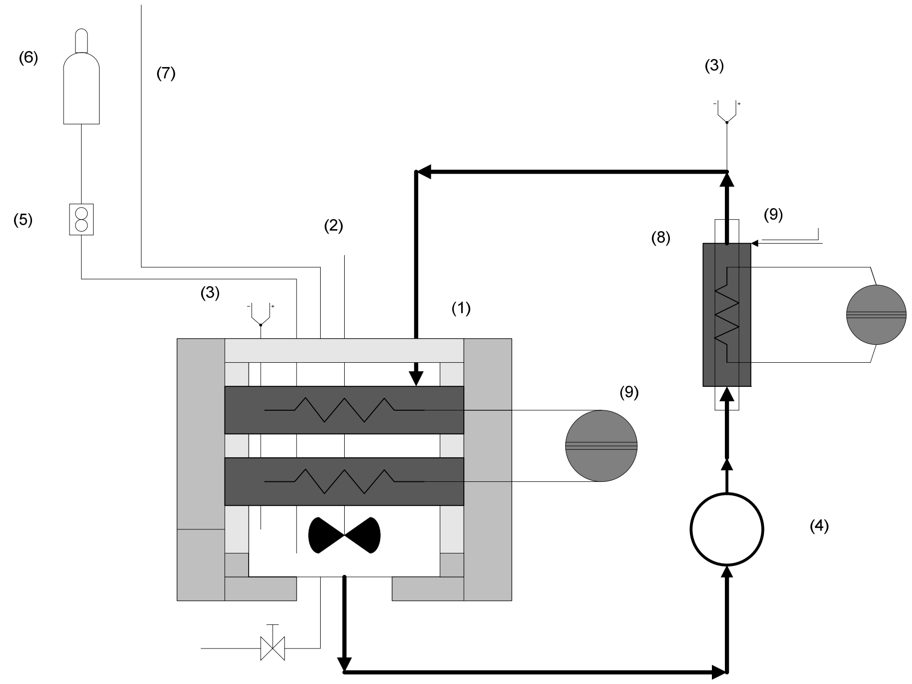

Figure 1. Loop reactor for lubricants synthesis

The results obtained in this loop reactor using H_2WO_4/SiO_2 as acid catalyst, were compared to the results obtained with a batch system and the performances were encouraging. For a kinetic study [3], runs at different temperatures and with catalysts differing in active specie concentrations (as amount of H_2WO_4 on SiO_2) were performed. The obtained results, collected in a loop reactor, were interpreted with a kinetic model, also including mass transfer effects, and the agreements between simulated curves and experimental points were satisfactory.

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INTENSIFICATION OF FLOW BLENDING TECHNOLOGY IN THE PRODUCTION OF MOTOR FUELS BY METHOD OF MATHEMATICAL MODELLING

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In current technologies of motor fuels production (gasoline, diesel fuel), the disregard of chemical interactons between separate components of the mixture (hydrocarbon flows, antiknock additives, oxygenates etc.) leads to discrepancy in calculated and experimentally determined on industrial units values of essential properties (octane number, freezing point etc.). The fundamental consequences of this are: a) quality deterioration of products – commercial gasoline, diesel fuel; b) decline in economic indicators due to overspending expensive components used in production. At large production capacity of commercial products manufacturing the economic indicators can reach considerable value. If the product in reservoir does not meet spesifications the correction of recipe is performed. This operation is time consuming and does not allow performing correction of the mixture during the blending process since obtaining the qualitive parameters of end product is only possible after putting all components into reservoir and their appropriate mixing.

New technology of flow blending anticipates preliminary calculation of flow rates of mixture components. The mixing operation is performed in accordance with preliminary determined flow rates and physical-chemical properties of deep petroleum refining products. Flow rates and properties of flows depend on hydrocarbon composition of raw materials and catalyst activity.

Experimental and theoretical studies of mechanisms, conditions and macroscopic regularities of catalytic processes for motor fuels production (naphtha reforming, isomerisation of pentane-hexane hydrocarbon cut, sulphuric acid alkylation of isobutane by olefins, hydrotreating, hydrodewaxing and catalytic cracking of heavy petroleum feedstock) made it possible to solve the multifactorial problem of intensification of motor fuel production technology using the method of mathematical modelling. The models development was performed on physical-chemical basis, namely taking into account thermodynamics and kinetics of hydrocarbon conversion on catalyst surface, as well as non-stationarity of processes due to coke deposition, catalyst ageing and catalyst poisoning by harmful contaminants, change in feedstock composition. To perform complete qualitative and quantitative analysis it is necessary to see interrelation between producing and modes of units operation, their influence on productivity of compounding. In this case the recommendations for change in recipes in order to increase the efficiency of blending stage will be correct and reasonable.

In production of motor fuel components the catalysts based on precious metals are used (Pt, Pd etc.). Reloading of fresh catalyst costs several dozens and hundreds of millions of dollars. At that the dependence on import of catalysts in petroleum refining is more than 70 %. The increase of catalyst service life on the units having high unit capacity allowed significantly decreasing in cost of gasoline and diesel fuel. In the frame of this direction the new technology of motor fuel production was developed, which was implemented on a variety of petroleum refining enterprises and does not have domestic analogues, as well as serves as an example of import substitution in the field of software for ensuring large industrial facilities.

The new technology of gasoline production allows decreasing in prime cost at saving the quality of RON-95, RON-98 gasoline that meets Euro-5 standard, this allows reaching economic effectiveness.

The determination of optimum technological modes depending on the fuel grade (summer, winter, arctic) taking into account chemical interreactions between hydrocarbons increases the yield of gasoline cut on 1 355 794 tonnes per year, Δ yield of gasoline = 55 575 tonnes per year. The yield of diesel cut is 375 593 tonnes per year, Δ yield of diesel fuel = 102 119 tonnes per year.

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COKE FORMATION REDUCTION IN THE CATALYTIC REFORMING REACTORS BY OPTIMAL WATER AND CHLORINE FEED IN THE REACTION ZONE

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The most important condition for the optimal exploitation of the bifunctional reforming catalysts is a balance of acid and metal activity. Organochlorine compounds are fed to the reactor unit, transformed into hydrogen chloride, enhance the selectivity of hydrocarbon conversion at the surface and thereby increase the depth of processing the hydrocarbon feedstock.

Temperature and quantity of promoters (organochlorine compounds and water) which are fed into reactor unit are the main control parameters which influence the activity of the catalyst during the feed cycle. The amount of chlorine on the catalyst surface is determined by the thermodynamic equilibrium of the chemisorption of chlorine atoms and depends on the hydrogen chloride and water molar ratio in the reaction zone, the temperature of the catalyst bed, and the degree of catalytic surface deactivation as a consequence of coking, poisoning and aging. To improve the resource efficiency of reforming reactors a methology of a chlorine amount calculating considering the variability of the hydrocarbon composition and catalyst activity changes is needed.

Reforming units industrial operation experience has shown that chlorine deficiency is the cause of catalyst activity decreasing in such important reaction as isomerization reactions of alkanes, which negatively influences the quality of the produced reformate. The chlorine loss from the catalyst surface also leads to the deactivation of the platinum centers acceleration, and hence to catalytic activity loss in the dehydrocyclization of paraffins and the process selectivity decreasing. On the contrary, an excessive amount of chlorine can cause an catalyst acid activity increasing and, consequently, the paraffins hydrocracking reaction acceleration that will cause a process selectivity reduction, the proportion of light hydrocarbons (methane and ethane) increasing in the circulating hydrogen-containing gas and increased hydrogen consumption.

To determine the mechanism of water action on the process with Gaussian'03 and HyperChem software using, based on the method of quantum-chemical modeling the thermodynamic analysis of conversion reaction of water coke-containing structure was done using the reaction: $C_{28}H_{14} + 28H_2O = 28CO + 35H_2$. The equilibrium concentrations of CO and H_2 are expressed through the initial concentration of water and the degree of conversion.

According to this methology, the reaction equilibrium constant and the conversion degree of the coke-containing water amorphous structure in the working temperature range from 753 to 773 K.

The catalytic reforming unit L-35-11/600 data are used for calculations: optimal water supply at the beginning of cycle was 0.3 l/h, the optimal feeding chlorine was 1 ppm. This water and chlorine flow rates provide optimum water/chlorine molar ratio on the catalyst (Mw/x = 20). Calculations has shown that with the process temperature changes from 753 to 773 the conversion degree varies in the range of 5,1-7,13 %. It was found that each specific temperature corresponds to an optimum amount of water which is fed into the reactor to maintain maximum reaction conversion. In this case the water supply varies from 0.3 to 0.51 l/h. Feed of water is more or less then optimal amount leads to a desired product yield reducing. It is found that at a varying water flow rates it is necessary to control the feed of chlorine to the reactor to maintain an optimum water/chlorine molar ratio on the catalyst. According to the calculation results, an optimal flow rate of chlorine varies from 1 to 2 ppm. Herewith the calculations have shown that the amount of CO produced varies from 0.24 to 0.6 ppm, which is acceptable for the catalyst using.

POSTER PRESENTATIONS

REGENERABILITY OF Ni AND Rh BASED CATALYSTS IN OXIDATIVE STEAM REFORMING OF BIO-OIL

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Introduction. Hydrogen is considered one of the most promising clean energy carriers for the next future and its production from biomass has become a new hotspot [1]. Catalytic steam reforming (SR) of bio-oil (obtained by flash pyrolysis of biomass) is known as one the most economically feasible methods for producing highly pure hydrogen [2]. Nevertheless, steam reforming is highly endothermic and requires supplying large quantity of energy. The oxidative steam reforming (OSR) is an attractive alternative to SR, because the heat generated in the exothermic oxidation promotes the endothermic SR reaction [3]. The regenerability of the catalyst is a key factor for the industrial implementation of the process, because the unavoidable catalytic deactivation by coke deposition makes it necessary the operation under reaction-regeneration cycles. This work compares the regenerability of two different catalysts (Ni and Rh based catalysts) in oxidative steam reforming of bio-oil.

Experimental. The experiments were carried out in a MicroActivity Reference equipment (PID Eng & Tech) with two steps (thermal+catalytic) in-series. The thermal step consists on a U-shaped tube (at 500 °C) that retains the carbonaceous solid (pyrolytic lignin) formed by re-polymerization of some bio-oil oxygenates during its volatilization, which minimizes operating problems and attenuates catalyst deactivation [4]. The volatile stream leaving the thermal step (oxygenates in bio-oil and water added to attain a desired steam/carbon molar ratio) was transformed in the second step (fluidized bed reactor) by catalytic oxidative steam reforming. Ni/La_2O_3-αAl_2O_3 (10 wt % Ni, 10 wt % La_2O_3) catalyst was prepared by incipient wetness impregnation method [4] and Rh/CeO_2-ZrO_2 (Rh/ZDC, 2 wt % Rh) catalyst was supplied by Fuel Cell Materials. The operating conditions were: 700 °C, steam/carbon molar ratio = 6, oxigen/carbon molar ratio = 0.67 and W/F_0 = 0.15-0.3 $g_{catalyst}h/g_{bio\text{-}oil}$. The catalyst regeneration consisted on coke combustion with air (650 °C for 3 h).

Results. The evolution of bio-oil conversion and H_2 yield with time on stream in two succesive reactions cycles (with intermediate regeneration) is shown in Figures 1a and 1b for the Rh/ZDC and Ni/La_2O_3-αAl_2O_3 catalysts, respectively. A complete conversion and nearly 90 % H_2 yield are achieved at zero time on stream for Rh/ZDC in the first reaction cycle and this values were steady for one hour. Subsequently, the catalyst attains another pseudosteady state ($X_{bio\text{-}oil}$>90 %, H_2 yield ≈ 70 %) and after 2 hours of time on stream, the catalyst activity decreases drastically approaching the values obtained by thermal routes. After the regeneration step, the initial reaction indices in the 2nd reaction cycle return to pseudosteady state values. Therefore, Rh/ZDC catalyst is largely regenerated in these conditions, although the initial values of bio-oil conversion and H_2 yield are not fully recovered.

On the contrary, Ni/La_2O_3-αAl_2O_3 catalyst suffers a very noticeable irreversible deactivation, since the inicial values of bio-oil conversion and H_2 yield in the 2nd reaction cycle are much lower than those in the 1st reaction cycle (100 to 82 % and 88 to 23 % from first to second reaction step). The main reason is a high decrease in Ni surface species (determined by XPS analysis of the regenerated catalyst), which probably migrates towards inner locations inside the particle which are not accesible to reactants.

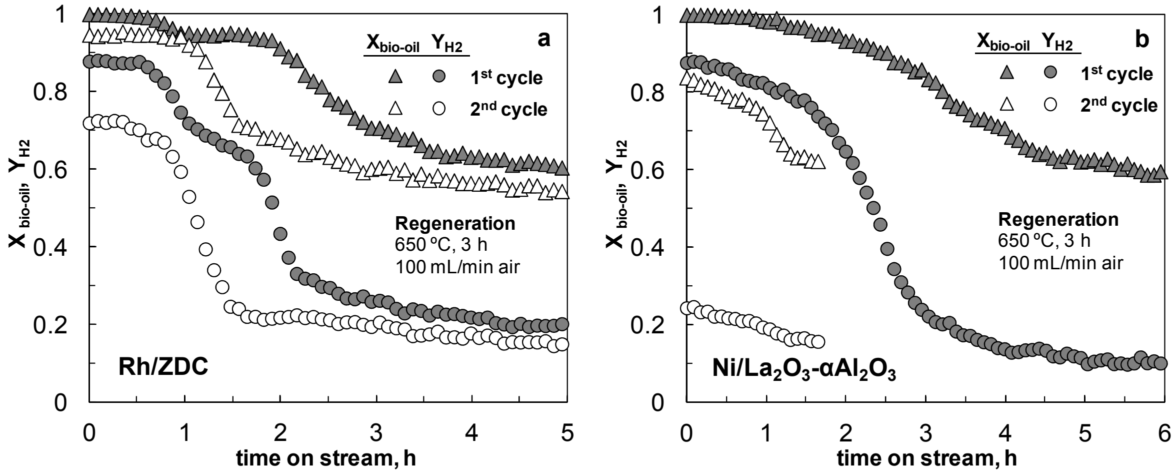

Figure 1. Evolution with time on stream of bio-oil conversion and H_2 yield of Rh/ZDC catalyst (a) and Ni/La_2O_3-αAl_2O_3 catalyst (b) in reaction-regeneration cycles in OSR of bio-oil

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PILOT-SCALE STUDY OF ETHYLENE SYNTHESIS BY ETHANOL DEHYDRATION ON ACID-MODIFIED ALUMINA CATALYSTS

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Bioethanol coming from lignocellulosic biomass could play an important role in the future as a primary feedstock in the chain of possible organic chemicals based on renewable materials. As a key intermediate, bioethylene produced from bioethanol can secure the downstream synthesis of a number of valuable products such as PE, PVC, glycols, ethylene oxide, etc. Ethanol can be converted into ethylene by catalytic dehydration using a variety of catalysts, preferably alumina ones [1, 2].

The present work was focused on the experimental study of ethylene synthesis by ethanol dehydration: started from the search for the catalysts, ended by the pilot-scale process study. The proprietary technique of hydrargillite (or gibbsite) centrifugal thermal activation (CTA) in TSEFLAR™ apparatus [3] is considered as environmentally friendly and economically attractive. Preliminary, a set of alumina-based catalysts prepared after CTA technology has been studied on the laboratory setup at 0.27-0.6 s and 375-400 °C. Of them, the HNO_3-modified Al_2O_3 was selected as the most active and stable catalyst. The acid-modified alumina catalysts in the form of ∅4 mm cylinders and ∅1.6 mm trilobes were used for ethylene synthesis in the pilot-scale setup with U-tube fixed-bed reactor, ID = 28 mm, L = 2800 mm. Process conditions were varied within: ethanol feed 1.5-2.5 kg/h, thermostat temperature 390-450 °C, catalyst bed height 0.65-1.2 m.

The best results were obtained at the residence time 2.4-3.0 s and the thermostat temperature 405-420 °C, the ethylene selectivity was as high as 97.6-98.6 % mol, and the consumption index of ethanol to ethylene was as low as 1.64-1.73 kg/kg.

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PRODUCTION OF BIO-ETHANOL FROM CELLULOSE-CONTAINING AGRICULTURAL RESIDUES ON THE PILOT SETUP

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A raw material of feedstock should be renewable rather than depleting, wherever technically and economically practicable. The 2nd generation bioethanol-from-agricultural-residues technology is much more energy-saving and environmentally friendly. Thereupon, the oats hulls, which constitute 28 % of the grain mass and contain up to 35 % of cellulose can be regarded as the most prospective raw material for bioethanol production.

In this work, bioethanol production from the oats hulls was studied on the pilot-scale setup which consisted of three main stages: (1) chemical pretreatment; (2) simultaneous saccharification and fermentation to 2,1 % crude bioethanol; (3) rectification to 92-96 % bioethanol.

The pretreatment was performed in rotary pulsed apparatus (RPA) and 100 L stainless steel reactor, equipped with stirring and heating systems. The suspension of oats hulls in a 2 % alkaline solution was circulated in RPA.

Simultaneous saccharification and fermentation was performed in 63-L reactor. The concentration of reducing sugars in the enzymatic hydrolysate obtained from the oats hulls fibrous product was found to be 35.5 g/L according to spectrophotometric measurements. Bioethanol was synthesized using the *Saccharomyces cerevisiae* Y-1693 producer. The mass yield of bioethanol was 94.1 % of the concentration of reducing sugars or 48.6 % of the substrate mass.

Finally, the bioethanol produced on the pilot setup was rectified and then tested in catalytic dehydration to ethylene. Overall consumption indexes obtained on the pilot-scale setups were rather optimistic: 95-98 kg of anhydrous bioethanol per 1 tone of oats hulls; 1.75-1.85 kg of bioethanol per 1 kg of ethylene, or 55-60 kg of ethylene per 1 metric ton of oats hulls. These figures demonstrate that bioethanol produced by enzymatic fermentation of the oats hulls may be successfully applied to ethylene synthesis.

CATALYTIC OXIDATIVE CONVERSION OF ETHANE TO ETHYLENE. DEVELOPMENT OF A PROCESS TECHNOLOGY

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Current industrial processes for ethylene production are based on highly energy-intensive steam cracking or catalytic dehydrogenation of hydrocarbon feedstock at temperature more then 850 °C yielding ethylene 25-30 % from naphtha and at about 50 % from C2-C4 alkanes.

The goal of the present study is development of the basis for generation a new catalytic technology for ethylene production from ethane. Therein we report the data on the catalyst optimization, reaction kinetics and reactor modeling as well.

Various oxide catalysts on the base of molybdenum and vanadium have been used. As the catalyst composition become more complex – from individual oxides to the binary ones and mixed VMoTeNbO eventually, ethylene yield increases approaching the acceptable for commercial application value – no less then 70 %.

Kinetic study allows specifying the impact of reaction conditions on catalytic performance. Longevity test during 500 h at 400 °C in reaction mixture 15 % vol. C_2H_6 in air have confirmed the stability of the catalyst developed. Within 360-450 °C temperature was determined does not affect the selectivity to reaction products at the equal value of ethane conversion. Therefore, multi-tubular reactor was chosen to implementation the process of oxidative dehydrogenation ethane on VMoTeNbO catalyst. The characteristics and process parameters for industrial tubular fixed bed reactor for ethylene production from ethane at capacity of 1,000 TPA are determined by using the two-dimensional pseudo-homogeneous mathematical model.

Thus, the process developed is capable of ensuring high ethane conversion at temperature lower 450 °C together with high selectivity to ethylene and in doing so it causes the significant reduction of energy consumption and increase an efficiency of the process in whole.

Acknowledgements

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PP-5

ENZYMATIC BUTANOLYSIS OF JOJOBA OIL. AN OPTIMIZATION STUDY

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Using the biorefinery concept, in this work, the enzymatic butanolysis of jojoba oil (JO) have been carried out to give mixtures of jojobyl alcohols (JA) as main product and fatty acid butyl esters (FABE) as co-product.

When the reaction took place the JA (9-octadecenol, 11-eicosenol, 13-docosenol and 15-tetracosenol), were obtained through two crystallizations steps. JA have pharmaceutical applications. After the separation step, the main properties as biodiesel of FABE were determined.

The synthesis of the JA and FABE over the Novozyme 435® has been developed and optimized following the Factorial Design and Response Surface Methodology. A full three-factorial design has proved effective in the study of the influence of the variables (selected for the present study temperature, alcohol/oil molar ratio and enzyme concentration) on the process.

The range studied was 63 °C and 77 °C for temperature, and 3 % wt and 7 % wt for the catalyst concentration, 4:1 and 8:1 for alcohol/oil molar ratio. Catalyst concentration has been found to be the most significant factor on the transesterification process and its influence is positive. The Response Surface model obtained, representing the yield of FABE, has been found to describe adequately the experimental results obtained.

Keywords: Jojoba oil; Jojobyl alcohols; Enzymatic Butanolysis, Optimization

A SYSTEMATIC METHODOLOGY FOR THE VIRTUAL RECONSTRUCTION OF OPEN-CELL FOAMS

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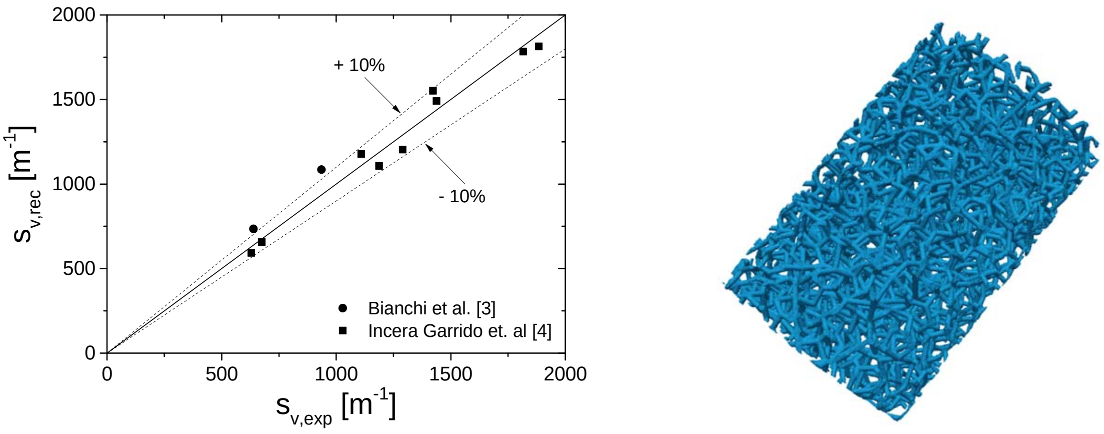
Open cell foams – cellular materials made of interconnected solid struts which enclose void regions – are recently receiving growing attention as innovative catalyst supports. High specific surface areas and high void fractions make foams very attractive as enhanced catalyst carriers, particularly for processes strongly limited by external mass and heat transfer [1]. Our understanding of the transport properties of such structures, however, is still very poor [2]. This scenario is hampering a large-scale industrial application of open cell foams in the field of catalysis. In fact, a fundamental analysis of these materials is required to fully characterize their properties and behavior. In this respect, Computational Fluid Dynamics (CFD) is a valuable tool to improve the understanding of open cell foams, being able to offer a deep insight in the complex flow field within the random tridimensional foam matrix. A CFD analysis requires however the accurate description of the foam microstructural geometry. Currently, digital reconstruction of the foam geometry is carried out by means of micro-computed tomography (μCT) or magnetic resonance imaging (MRI). These expensive and time-consuming methods enable the reproduction of a single portion of the investigated sample, which might be not fully representative of the foam features. To overcome these problems, the aim of the present work is the development of an automatic numerical procedure that can generate a realistic random foam structure, to be used for CFD simulations. Our approach is based on the following workflow: first, a random bed of spheres of fixed size is packed using a Discrete Element Method. Each sphere is substituted by a polyhedral unit cell whose features rely on the geometrical characteristics of real foams. Once the foam skeleton has been established by placing cells, the vertices of the polyhedral cells are moved to ensure a continuous solid matrix by means of the overlap among struts. Moreover, a strut profile taking into account both the shape of the cross-section and the solid clustering at the nodes is proposed. The foam microstructure obtained by our approach resembles the real foam geometry, see Figure 1b, with respect to both the random pore distribution and the fully interconnected solid matrix. Several foam samples have been generated to validate the procedure by comparing the geometrical properties of the generated foams with μCT data from the literature [3, 4]. The deviations of the specific surface area between virtual foams and experimental data are less than 10 %, see Figure 1a. Moreover, pressure drop simulations have been carried out to investigate the flow field established inside the reconstructed foams: ΔP predictions show good agreement with experimental data.



(a) **(b)**

Figure 1. Specific surface areas of reconstructed foams versus experimental measurements (a), and virtual reconstruction of a foam sample (b)

Thus, the proposed methodology can reproduce open cell geometries with a promising accordance with specific surface areas, morphological and flow features of real foams. On a more general basis, our methodology enables the computational analysis of the heat and mass transport processes prevailing in foams over a wide range of operating conditions even not accessible by experiment. Moreover, the foam generation procedure is an excellent tool for the rational design and the optimization of these structures, enabling a parametric analysis of the foam transport properties.

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PP-7

A GREEN APPROACH FOR THE SIMULTANEOUS REMOVAL OF ARSENIC(III) AND CHROMIUM(VI) IN AN AQUEOUS MEDIUM BY ATMOSPHERIC PRESSURE PLASMA JET

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An atmospheric pressure plasma jet reactor was designed and tested for the redox transformations of As(III) and Cr(VI) in aqueous medium. As(III) and Cr(VI) showed promising synergistic effect at various pH 2-7. Active species hydrogen peroxide (H_2O_2), hydroxyl radicals (•OH), hydrated electrons (e^{-}_{aq}) formed in the discharge were quantified. Typical data, as shown in Fig. 1 confirmed that the optimal pH for As(III) oxidation by Cr(VI) is 4.0, whereas the best Cr(VI) reduction was achieved at 2.0. It has been observed that H_2O_2 undergoes decomposition to generate •OH, which oxidizes As(III) to As(V). The presence of both the reactants complement the redox nature, where As(III) suppresses the re-oxidation of Cr(III) to Cr(VI). Adding Fe(II) salts to the reaction mixture significantly enhanced the As(III) oxidation and also arsenic immobilization by forming co-precipitation with Fe(III) ions. The presence of hydroxyl scavengers retarded the target reactions. Influence of concentrations and applied voltages was studied for individual/simultaneous removal of the reactants and the best energy yield obtained for As(III) and Cr(IV) was ~22 g/kWh and ~18 g/kWh respectively. This study highlights the potential of plasma jet in removing the heavy metals As(III) and Cr(VI) from waste water.

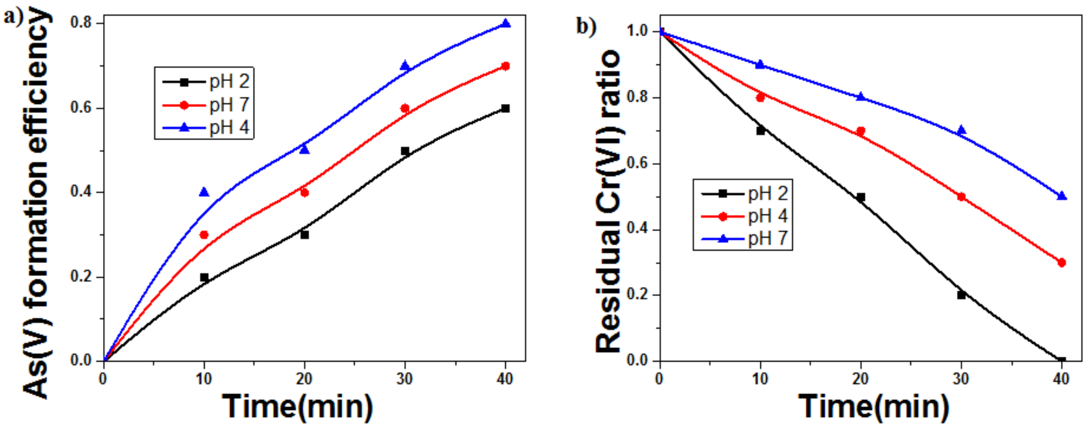

Fig. 1. (a) As(III) oxidation (b) Cr(VI) reduction with plasma jet at various pH (voltage 18 kV, Argon flow 300 sccm, As(III) concentration: 1 mM and Cr(VI) concentration: 0.6 mM)

PP-7

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GAS QUENCHING PROCESS OF JET IN CROSSFLOW FOR THE PARTIAL OXIDATION OF NATURAL GAS TO ACETYLENE

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The partial oxidation (POX) of natural gas is the major process for the production of acetylene and synthesis gas, which requires quick quenching to get the maximum yield of acetylene [1]. In this work, a novel quenching process was proposed, in which the cold product gas being used as quenching medium was injected into the crossflow of the high-temperature pyrolysis gas. As a result, the pyrolysis gas was quenched from 1800 K to 900 K in 2-3 milliseconds, and then the heat of the mixture gas was recovered to generate steam.

The computational fluid dynamics (CFD) coupled with detailed reaction mechanism Leeds 1.5, which has been verified by simulations of the industrial POX process [2,3], was used to simulate the mixing and quenching performance. Both the Probability Distribution Function (PDF) and Eddy Dissipation Concept (EDC) models were used to compute the chemistry source term. The mixedness, temperature and species concentrations were investigated during the quenching. The results showed that the uniform index was higher than 97.5 % and the mixing temperature decreased below 900 K after 300 mm from the jet position, as shown in Fig. 1. The dimensionless concentrations of the major species C_i/C_0, where C_0 is area-weighted average mass fraction in the jetting cross-section, are shown in Fig. 2. The dimensionless concentration of C_2H_2 was higher than 0.976, indicating that the loss ratio of acetylene was less than 2.4 % in the quenching process. Accordingly, the concentrations of C_2H_4 and C_2H_6 increased because C_2H_2 was hydrogenated to C_2H_4 and C_2H_6. The gas quenching process is feasible because a high acetylene yield was obtained and the heat could be effectively recovered. It is promising to replace the water quenching process used in the present industrial POX process.

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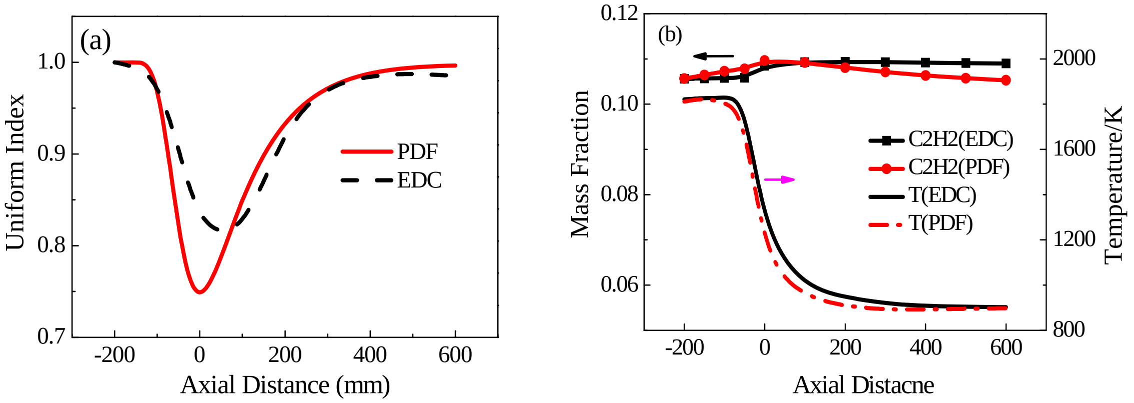

Fig. 1. Axial profiles of (a) mixing and (b) C_2H_2 concentration and temperature

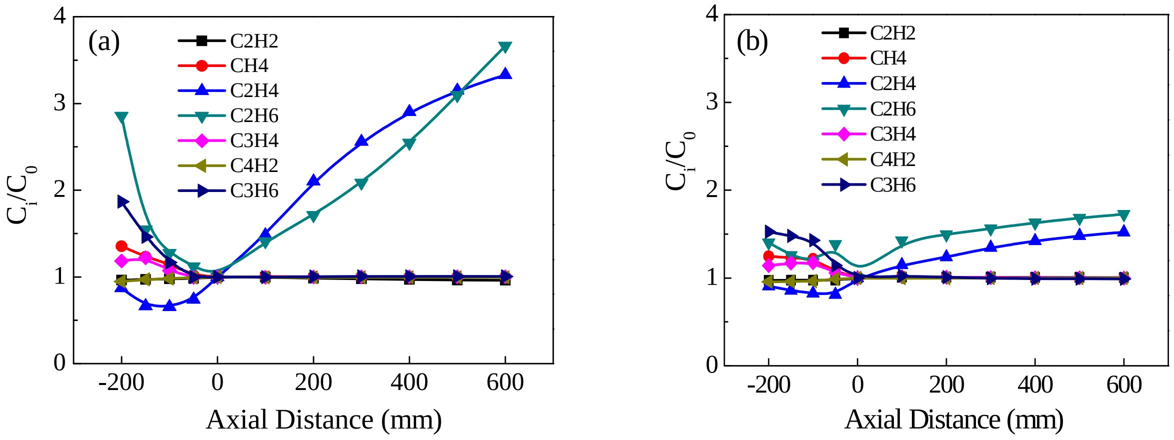

Fig. 2. Axial profiles of dimensionless concentrations of major species calculated with (a) PDF and (b) EDC models

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CATALYTIC HYDROCONVERSION OF BENZENE CONTENT FRACTION IN REFORMING REACTORS

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According to modern ecological standards benzene content in the finished motor gasoline is strictly restricted due to its high toxicity level. Benzene primary enters in the finished motor gasoline with of catalytic reforming stream. The decrease in benzene content in catalytic reforming product stream can be provided by primary feedstock fractionating or extraction of the benzene content fraction from reformate. However this approach leads to decrease in capacity level and produce extra low octane streams. In connection therewith the actual problem is an implementation in the oil refinery plant processes of benzene fraction extraction from reformate with a following catalytic hydroconversion on bifunctional catalyst.

This paper is dedicated to design and improvement of the catalytic hydroconversion technology in reformer reactor at Komsomolsk Oil Refinery Plant. Catalytic benzene hydroconversion process can pass on Pt-Re balanced reformer catalysts on Al_2O_3 base at following operating parameters [1-2]:

Process Temperature:	130 °C;
Pressure:	3.0 MPa;
Volume Feedstock Rate:	1.0 h^{-1};
HBG / Feedstock Ratio:	300 nm^3/m^3.

In this case benzene catalytic hydroconversion can be conducted in reactor R-3 (fig. 1) of the reformer plant L-35-11/450K, with non-significant changes in the material streams direction.

Hydrotreated feedstock is mixed with hydrogen-bearing gas (HBG), is entered into furnace F-1, is heated to the process temperature and then the hot feed vapor is sent to the reformer reactor R-1. Gas-product mixture after R-1 is heated again in the second chamber of furnace F-1 and is sent to reactor R-2. The mixture is then heated in the F-1 fourth chamber and is sent to reactor R-4. The reactor effluent is sent to the stabilization column C-1.

PP-9

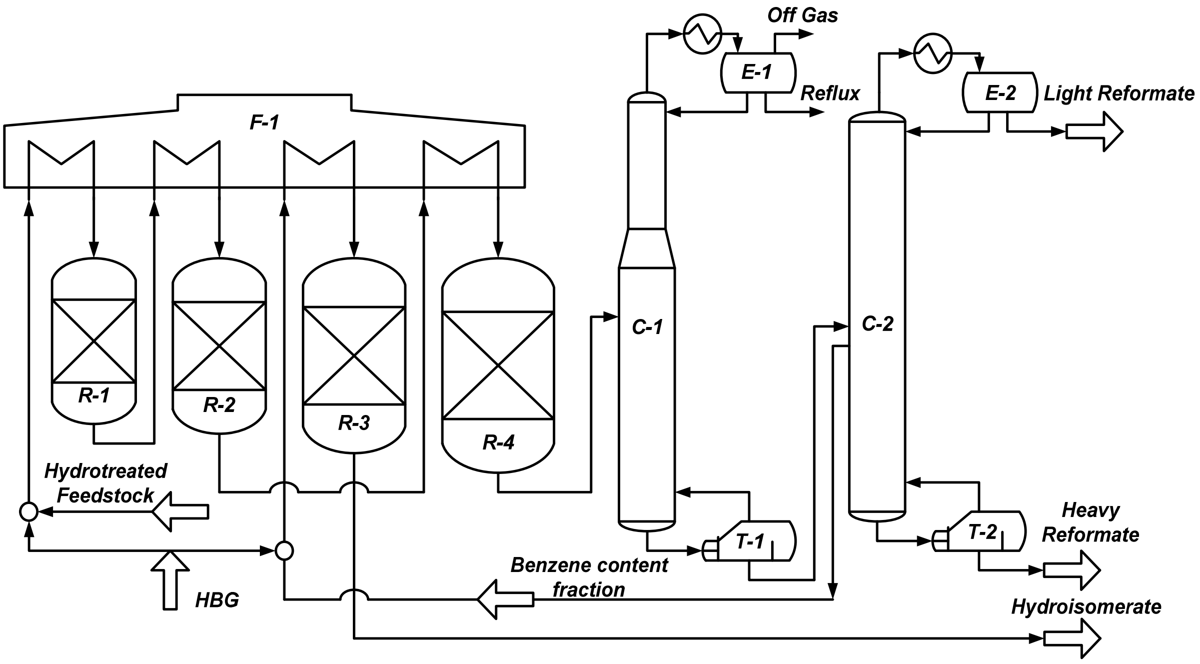

Fig. 1. PFD of catalytic reformer with catalytic hydroconversion unit of benzene content fraction

The off gas and reflux, which are formed due to side reaction, are separated overheads C-1. The off gas is exported to the fuel gas system and reflux is sent to gas fractionating unit for further treatment. The stabilized reformate is exported to the fractionating column C-2. The benzene content fraction is separated out as a sidecut stream and exported to R-3 reactor, where catalytic hydroconversion process is conducted.

Involving the catalytic hydroconversion product into motor gasoline blending process allows to decrease capital costs for production of Regular - 92 and Premium – 95 motor gasoline on 8.4 and 6.4 % appropriately. This effect is reached by decreasing high cost components content (MTBE) in gasoline pool and reduction of finish motor gasoline quality margin.

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APPRAISAL OF FCC- AND ACTIVATED CARBON-BASED CATALYSTS FOR THE HYDRODEOXYGENATION OF RAW BIO-OIL USING MILD CONDITIONS

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Introduction. Biomass is becoming an important source of chemicals and energy. Bio-oil (liquid product of flash pyrolysis of lignocellulose) in particular drives great attention due to its prospect of becoming a sustainable source of chemicals and fuels. However, the use of bio-oil as a fuel is subjected to an upgrading treatment to overcome its main drawback: the oxygen content [1]. Hydrodeoxygenation (HDO) offers the possibility of oxygen removal, obtaining a second-generation biofuel [2], requiring relatively harsh conditions (>200 bar, >300 °C) and expensive catalysts like noble metals supported ones (Pt, Pd, Ir…). Activated carbons (AC) obtained from biomass wastes are interesting supports for HDO catalysts due to their hydrothermal resistance [3], and to their high acidic sites density. In this work, we have compared the performance of Pt-Pd/FCC and /AC catalysts during the HDO of raw bio-oil.

Experimental. Bio-oil was obtained by fast pyrolysis of black poplar sawdust in a conical spouted bed reactor at 450 °C. The AC support was synthesized from olive stone (OS) waste, which was impregnated with H_3PO_4 85 wt % with an impregnation rate (wt H_3PO_4/wt OS) of 3, and carbonized up to 500 °C at 10 °C min^{-1}. The catalysts were characterized by N_2 adsorption–desorption isotherms, FTIR spectroscopy of pyridine adsorption, and ammonia adsorption–desorption (TPD). HDO reactions were carried out in a down-flow fixed bed reactor of 15 cm^3: WHSV, 2.6 h^{-1}; 450 °C; 65 bar; H_2/Oil ratio, 2000 vol. % and TOS, 0-8 h. Gases were analysed on line using a MicroGC, dividing them in gas, LPG and CO+CO_2. Liquids were collected and separated in an aqueous fraction, which was analysed in a GC-MS; and in an organic fraction, analysed in a GCxGC-MS. Water content in the aqueous fraction was determined by means of Karl-Fischer titration and the aromatic and aliphatic compounds were characterized by FTIR spectroscopy.

Results. AC catalyst exhibits a well-developed micro and mesoporosity with 1305 $m^2\,g^{-1}$ BET surface area and a total acidity of 150 $\mu mol_{NH_3}\,g^{-1}$, whereas FCC catalyst shows 52 $m^2\,g^{-1}$ and 47 $\mu mol_{NH_3}\,g^{-1}$ respectively. In terms of gas, liquid and solid (coke) yields both catalysts have equivalent activity. Figure 1 shows the water content of the aqueous phase liquid product, which can be correlated with the HDO conversion assuming the simplified reaction: $R{=}O + 2H_2 \rightarrow H\text{-}R\text{-}H + H_2O$. As seen, AC catalyst allows for removing higher amounts of oxygen from the bio-oil while keeping this activity for longer, which also coincides with higher yield of aromatics in the organic phase. Furthermore, the higher amounts of steam for the AC catalyst is responsible for the lower deactivation while higher presence of aromatics (that has been stripped by the steam) in the organic liquid phase. These results could be attributed to the high stability of the AC catalyst in steam presence [4]. Besides, AC catalyst has higher selectivity of CO (valuable as a fuel), whereas FCC catalyst has higher selectivity of CO_2, which supposes a least carbon loss.

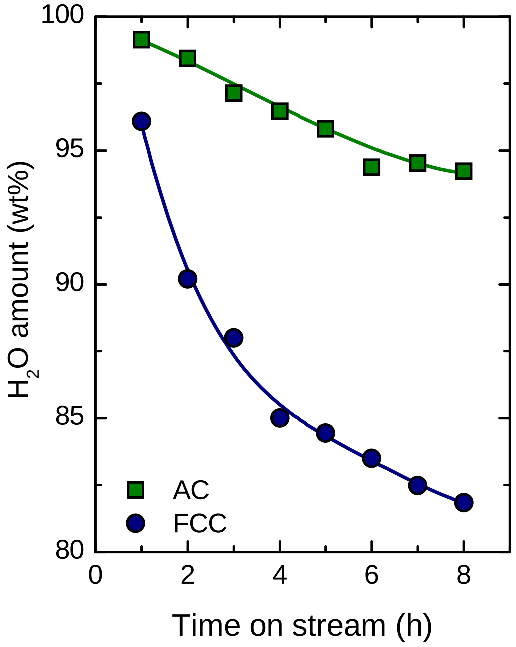

Figure 1. Water content in the aqueous phase

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AQUEOUS-PHASE REFORMING OF OXYGENATED HYDROCARBONS OVER NICKEL-BASED CATALYST IN A MULTIPHASE REACTOR FOR HYDROGEN PRODUCTION

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Introduction

Biorefineries integrate processes that produce chemicals, fuels, power and heat from lignocellulosic biomass by thermochemical routes including gasification, pyrolysis and catalytic routes, or by biotechnical routes such as fermentation. Biomass-based fast pyrolysis and Fischer-Tropsch reactions are alternative processes for fuel and chemical production from renewable biomass. In spite of the sustainable character of these technologies, the target products are accompanied by large water fractions with organic residues considered as waste streams. The disposal of these water fractions reduces the efficiency of the processes due to costly conditioning treatments, and upgradeable-product loss. To increase the process and product efficiency, the value of all streams should be maximized.

Currently, there is no efficient technology to utilize the diluted organic compounds in the water fractions of fast pyrolysis and Fischer-Tropsch processes. Catalytic aqueous-phase reforming (APR) is a highly potential route to convert the organic compounds included in these water fractions to products such as hydrogen and methane. To maintain aqueous phase in the reaction medium, APR is conducted at low temperatures (200-250 °C) and high pressures (20-50 bar) making APR a promising route to produce hydrogen with low CO concentration [1] by an energetically efficient process [2].

Experimental

Aqueous-phase reforming of 1-10 wt % oxygenated hydrocarbons was conducted over different nickel-based catalysts. The commercial Reformax330 was tested as reference catalyst. In addition, Ni and bi-metallic Ni-M (M = Cu, Ce, Sn) on activated carbon, silicon carbide, and mesoporous carbon (CMK-3) were synthetized and tested in APR. The catalyst was packed in the midsection of a tube reactor and reduced in situ with a N_2:H_2 = 1 mixture.

APR was conducted in a continuously operated tubular reactor. The operational conditions were temperatures ranging from 225 to 235 °C, pressure 2 bar above the vapour pressure of water at the set temperature, and weight hourly space velocity (WHSV) of 1-10,0 h^{-1}.

Results and discussion

The results of catalyst and operational-conditions screening were evaluated in terms of total conversion (X%), conversion to gases (CtoG%), production rate (PR), turn over frequency (TOF), yield (Y%), and selectivity (S%). Hydrogen and methane were the main gaseous products, and therefore, these were the main components considered to analyse the process performance. The results will be discussed and compared with previous works reported in literature.

Conclusions

Aqueous-phase reforming of oxygenated compounds, mainly glycerol and ethylene glycol, has been widely investigated over the last 10 years. However, challenges of the process, such as mass transfer limitations and low concentrations of the reactants, as well as performance and stability of catalysts still require considerable research effort.

Platinum-based catalysts supported in different metal oxides and carbonaceous materials have received considerable attention in literature due to high activity, and hydrogen selectivity of these catalysts. This study considers a less expensive nickel-based catalyst, and carbonaceous supports and metallic promoters to improve the stability and activity of the catalyst. As a result, a suitable catalyst and favourable operational conditions will be presented for selective production of hydrogen and methane.

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EFFECT OF HYDRODYNAMIC CONDITIONS ON LIQUID-PHASE OXIDATION OF CUMENE

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In the present work the effect of hydrodynamic conditions on the process of cumene liquid-phase oxidation was studied for the case of bubble reactors equipped with propeller or special self-priming stirrer. Experiments were carried out under static conditions by bubbling the air through the heated layer of hydrocarbon.

The highest rate and selectivity toward cumene hydroperoxide (ROOH) were achieved for bubble reactor with self-priming stirrer in comparison with traditional reactor (Fig. 1). It was shown that hydrodynamic conditions were not similar for bubble reactor equipped with stirrers of different design. These differences were probably associated with shape, sizes and moving rate of air bubbles. Kinetic curve of cumene hydroperoxide formation approached to the saturation for the case of the bubble reactor, while in case of bubble reactor equipped with self-priming stirrer cumene hydroperoxide formation takes place with constant rate up to concentration of 60 % wt.

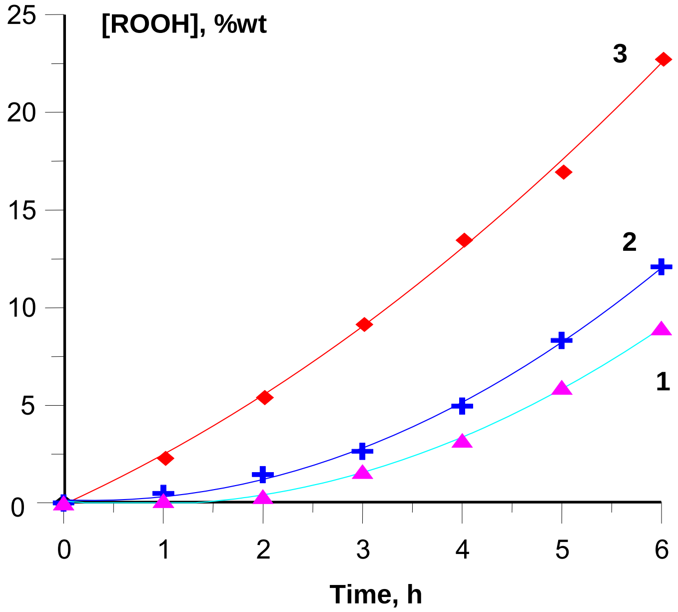

Fig. 1. Kinetics of cumene hydroperoxide formation in reactors:
1 – bubble reactor without stirrer, 2,3 – bubble reactor with propeller and self-priming stirrers, respectively temperature = 110 °C, V_{air} = 0.2 l/min

Selectivity toward cumene hydroperoxide decreased as cumene conversion increases. It is noteworthy that at similar conversions the selectivity toward cumene hydroperoxide was higher for the case of bubble reactor equipped with self-priming stirrer (Fig. 2). Moreover, this parameter increases with the rise of oxidation depth. Hence, hydrodynamic conditions influence on both cumene oxidation rate and ratio between the products formed.

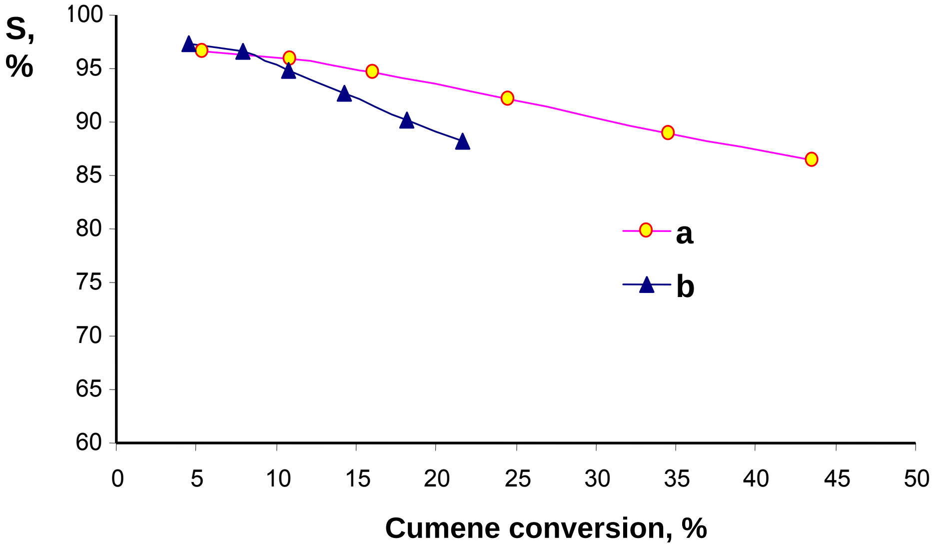

Fig. 2. Dependence of selectivity toward cumene hydroperoxide on cumene conversion for the bubble reactor with (a) and without self-priming stirrers (b) [dicumyl peroxide] = 0.01 mol/l, T = 110 °C, ω =3600 rounds per minute

Kinetics parameters, such as ($k_2/\sqrt{k_6}$) ratio representing the ratio between rate constants for chain growth and chain interruption and named as oxidability parameter, and activation energy were determined. The obtained activation energy was similar to those described in literature for various catalytic systems, and was amounted to 48.77 kJ/mol. It is noteworthy that the ratio between the rate constants ($k_2/\sqrt{k_6}$) was found to be practically two times higher in comparison with literature data. The reasons of these effects will be discussed.

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ELECTROCHEMICAL REACTOR FOR CONTINUOUS CO_2 VALORIZATION: SYNTHESIS AND USE OF Sn NANOPARTICLES ON GDEs

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Electrochemical reduction is an interesting possibility for the valorization of CO_2, especially attractive coupled with renewable sources such as wind or solar power, because it has been proposed as a way to store intermittent renewable energy in the form of chemical products. One of the most promising products is formate/formic acid, since it has been pointed out as a suitable fuel for fuel cells or renewable hydrogen carrier and it is widely use at industry as raw material. Recent research efforts focus on the development of Sn Gas Diffusion Electrodes (Sn-GDEs) which allow working at high current density with high faradaic efficiencies [1].

The aim of this work is to propose a method for synthetizing Sn nanoparticles (NPs), and to use these NPs deposited on GDEs for an electrochemical filter-press type reactor for continuous CO_2 electroreduction to formate following our previous research [2,3]. Sn NPs were synthesized using a solvothermal method and were characterized by TEM (Figure 1) and cyclic voltammetry. The size of the carbon supported Sn NPs was approximately 70 nm. Sn-GDE electrodes consist of a carbon paper as carbonaceous support, a microporous layer (MPL) and the catalytic layer (CL) formed by the Sn NPs. MPL and CL were deposited in form of inks with an airbrush. Sn-GDEs were also characterized by SEM (Figure 2) and cyclic voltammetry.

PP-13

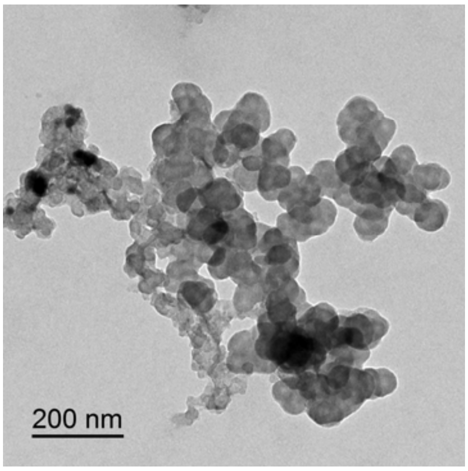

Figure 1. Sn nanoparticles TEM images

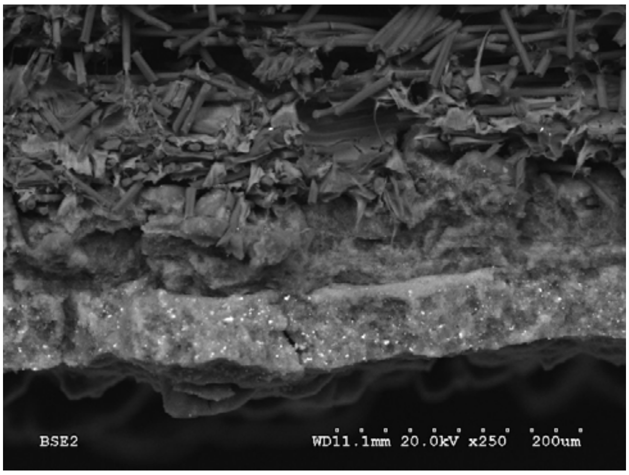

Figure 2. Sn-GDE SEM image

Electrodes were tested on a filter-press under different current densities and electrolyte flow. Using the prepared Sn-GDE it was possible to achieve a 70 % Faradaic Efficiency (FE) to formate at a current density of 150 mA cm^{-2}, obtaining a formate concentration of 2.5 g L^{-1} which outperforms the results obtained in previous studies. Increasing the current density and decreasing the electrolyte flow, it was possible to reach concentrations over 16 g L^{-1} but at the expense of a 42 % FE. Despite the high concentrations obtained, further research is required to keep high FE operating at high current densities.

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Acknowledgements

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Pd-SBA15 CATALYSTS PREPARED BY SPRAY DRYING FOR ABATEMENT OF CH_4 EMITTED BY CNG VEHICLES

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Compressed Natural Gas (CNG) engines have considerable advantages over conventional gasoline and diesel engines from an environmental perspective, by limiting the formation of NO_x. Moreover, NG contains only 75 wt % carbon versus 86-88 wt % of gasoline or diesel, giving rise to the production of less CO_2 per unit of energy released [1].

However, unburned methane is harder to oxidize than gasoline-derived unconverted HCs.

Commercial catalysts are mostly based on γ-Al_2O_3-supported Pd [2], but having at least three times the noble metal loading compared to that of conventional three-way catalysts. However, besides being expensive, the latter easily sinter. A possible overcoming solution could be the insertion of the noble metal in the structure of perovskite-type transition metal oxide mixtures. In this framework, ordered mesoporous molecular sieves can be considered as support for noble metal catalyst, due to their high surface area, pore volume and narrow pore size distribution. SBA-15 has here been used as support for Pd catalysts for abatement of methane emitted by CNG engines. Two different loading methods were compared: Incipient Wetness Impregnation (IWI) and Spray Drying (SD).

Spherical SBA-15 was obtained according to the procedure reported in our previous works [3]. Calcined SBA-15 was employed as supports for Pd (0-2 wt %). The mesoporous silica support and the supported Pd catalysts were characterized by means of XRD, BET, FESEM and STEM techniques.

The activity of the prepared catalysts was analyzed by temperature programmed combustion (TPC), by feeding a standard gas mixture (CH_4 = 0.4 vol %; O_2 = 2 vol %, N_2 = balance) at a constant rate to a fixed-bed microreactor.

The XRD characterization showed that the synthesized SBA-15 was amorphous, though the small-angle investigations showed ordered structures with pores displaced in a hexagonal way. The patterns of Pd-supported catalysts, both obtained by IWI and SD, did not show any change in the ordered structure with respect to the pure supports.

The surface characterization showed a specific surface area of 660 m^2/g for SBA-15, with a mean pore size of about 10 nm. The addition of Pd on the supports, both by means of IWI and SD, decreased the SSA of the catalysts, with values ranging between 540 and 590 m^2/g.

The catalytic activity results are reported in Figure 1.

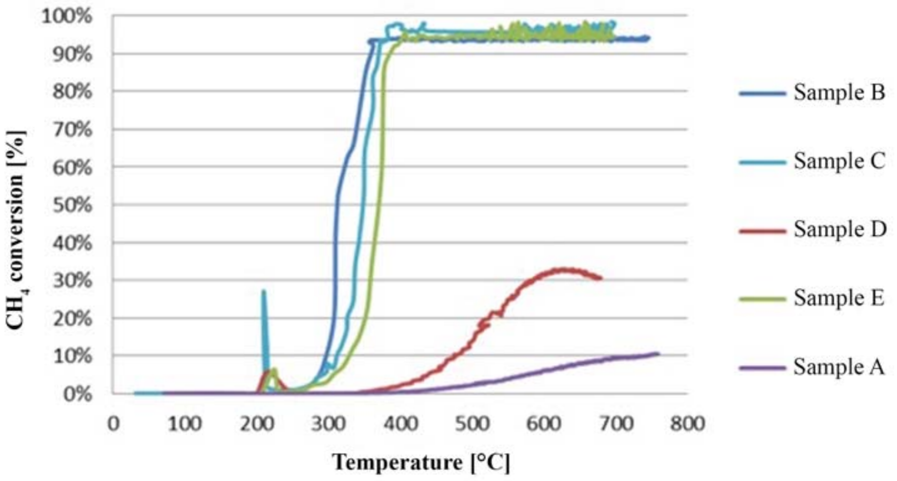

Figure 1. Catalytic activity of the developed catalysts

The pure support (sample A) did not show any methane conversion up to 750 °C. For all the catalysts, the addition of Pd allowed to obtain complete combustion of CH_4. For both impregnation methods, the complete conversion of methane was achieved at a temperature of about 400 °C. For the IWI method, the full conversion occurred with a Pd loading of 2 wt %, whereas the SD technique allowed to get the same catalytic performance and at the same time to cut by half the content of noble metal (sample C). The catalytic tests also proved that the spray drying parameters affected the Pd dispersion and consequently the catalytic activity. In fact, the Pd dispersion results less uniform by operating at higher pressure, and the catalysts showed a worse behavior, even by increasing the Pd loading up to 2 wt % (samples D and E).

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SORPTION ENHANCED STEAM METHANE REFORMING ON CATALYST/SORBENT BIFUNCTIONAL PARTICLES: A CFD FLUIDIZED BED REACTOR MODEL

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In this work, a pilot scale fluidized bed reactor is simulated for production of hydrogen by sorption-enhanced steam methane reforming (SE-SMR). The hydrodynamic behaviour of a 500 μm particle bed contained in a 25 cm ID vessel is simulated by means of a two-fluid Eulerian-Eulerian model. The bed is composed of bi-functional particles that act as catalyst and sorbent, simultaneosly: the calcined particles are composed of 10 % wt of Ni (catalyst), 60 % of CaO (sorbent for the CO_2 capture) and calcium aluminate as inert support.

The kinetics of steam methane reforming (SMR) and water−gas shift (WGS) are described by the model of Numaguchi and Kikuchi [1], while the grain model of Stendardo and Foscolo [2] is used for the carbonation reaction. Due to the relatively small size of particles, intra- and extra- particle mass transfer effects are comparatively small and are taken into account by means of a overall effectiveness factor for SMR. On the other hand, the sorption limiting step is simulated by a product layer CO_2 diffusivity that is a strong function of CaO conversion. The bifunctional particle model developed in a previous work [3] is used to extimate the effective reaction rates at the process temperature (650 °C), different CaO conversion level inside the particles and different bulk gas concentrations approaching the equilibrium values. The feeding gas composition is fixed at 25 % CH_4 and 75 % H_2O by volume. The particle model was validated by means of experimental tests, as described in a differet comunication to this Conference. These results are here implemented in a CFD model previously developed [4], in order to simulate the fluidized bed reformer/carbonator.

Simulations have been carried out at different superficial gas velocity within the bubbling regime, between 2 and 5 times the minimum fluidization velocity (~ 0.1 m/s) and for different static bed height in the range 20-40 cm, to evaluate the importance of various dynamic phenomena like by-passing of reactant gas through rising gas bubbles and contact time. Furthermore, the simulations are referred to several CaO conversions in the bed (between 0, completely calcinated, and 50 %) to describe different stationary conditions that could occur during steady state operation of the reactor.

Hydrogen mole fraction > 0.95 in the dry gas is predicted for superficial gas velocity up to 0.3 m/s and static bed of 40 cm. Furthermore, the bubble growth in the fluidized bed influences product yields and concentration oscillations are observed. It is worth noticing that SMR reaction extent is favoured in the bed bottom region of the reactor and on the whole methane is completely converted (close to equilibrium), while the CO_2 capture and related WGS reactions need longer contact time, so that they take place mainly on the remaining part of the bed. This can be observed in Figure 1 where a typical gas composition is shown along the bed (mole fractions on wet gas basis) for CH_4, H_2, CO, CO_2, at a superficial velocity of 0.3 m/s, initial bed height of 0.4 m and initial CaO conversion of 35 %. However, the concentration profiles also indicate that CH_4 and CO_2 are present at their maximun concentration in the same bed region (the central gas jet in the lower part of the bed), so that methane reforming and carbon dioxide capture reactions take place in considerable extent simultaneosly: the concept of combined catalytic and sorption functions is shown to be effective by these numerical findings. The strict combination of catalytic and sorption sites in one particle helps reducing diffusion paths and related resistences.

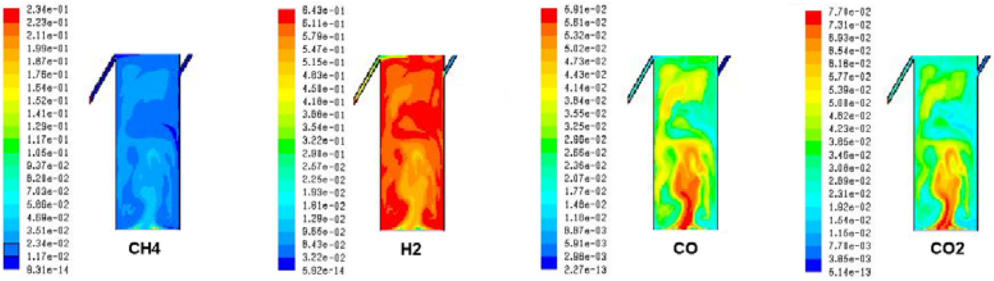

Figure 1 – mole fraction wet of the gas species in the fluidized bed

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Acknowledgements

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1-BUTENE OLIGOMERISATION: EFFECT OF SiO_2/Al_2O_3 RATIO ON HZSM-5 ZEOLITE

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INTRODUCTION

Oligomerisation of light olefins, such as 1-butene, is an interesting route for the production of higher molecular weight hydrocarbons to be used as fuels (e.g., gasoline, diesel) and lubricants [1]. In addition, 1-butene feedstock can be obtained from fluid catalytic cracking (FCC) or from more sustainable sources (e.g., biomass or polyolefinic wastes of consumer society) [2].

EXPERIMENTAL

The catalysts studied are based on HZSM-5 zeolites (supplied by Zeolyst Int.) with different SiO_2/Al_2O_3 ratios (30-280). Zeolites have been agglomerated with pseudobohemite (30 wt. %) as binder and Al_2O_3 (20 wt. %) as inert charge that confers a matrix with meso-and macropore structure to the catalyst.

The catalysts have been characterized by nitrogen adsorption-desorption (ASAP Micromeritics 2000) in order to determine the micropore volume and BET surface area (Table 1). Acid properties have been determined by DSC-TPD of ammonia.

The catalytic tests were performed in an isothermal fixed bed reactor at the following operating conditions: 275 °C; atmospheric pressure; 1-butene partial pressure, 70 %; space time, 6 (g of catalyst) h (mol of $CH_2{}^{-1}$); time on stream, 10 h. The products obtained are divided in gases, analysed on-line in a gas chromatograph (Micro-GC Agilent 3000A), and in liquids, analysed at the end of the reaction by gas chromatography (GC-MS QP2010S Shimadzu).

Table 1. Physical and acid properties of HZSM-5 catalysts

SiO_2/Al_2O_3	S_{BET} (m_2 g^{-1})	V_{micro} (cm_3 g^{-1})	Total Acidity (mmol NH_3 g zeolite^{-1})	Acid strength (kJ mol NH_3 $^{-1}$)
30	408	0.134	0.77	125
80	448	0.129	0.43	116
280	408	0.092	0.12	81

The criteria used for assessing the performance of the catalysts were: i) conversion; ii) yield and selectivity of each lump of products (C_3H_6, C_4H_{10}, C_5-C_7

paraffins, C_5-C_7 olefins, C_8-C_{12} paraffins, C_8-C_{12} olefins), and; iii) deactivation by coke deposition.

RESULTS AND DISCUSSION

The Figure 1a shows the effect of SiO_2/Al_2O_3 ratio on product selectivity at zero time on stream. It should be noted that catalyst acidity plays an important role in the oligomerisation of 1-butene. The selectivity of C_8-C_{12} oligomers decreases with an increase in SiO_2/Al_2O_3 ratio.

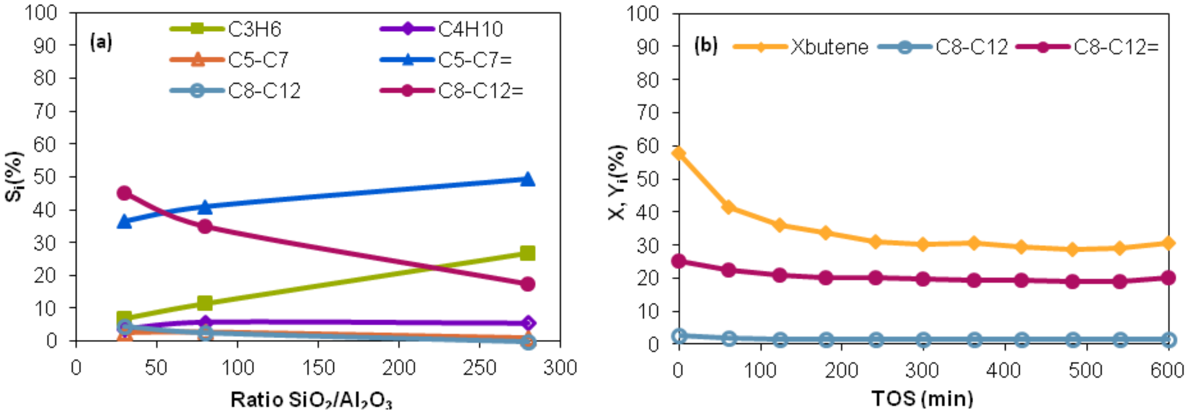

Figure 1. Evolution of the products selectivity with the SiO_2/Al_2O_3 ratio at zero time on stream (a) and evolution of the conversion and C_8-C_{12}, C_8-$C_{12}^{=}$ yield for HZSM-5 catalyst (SiO_2/Al_2O_3 = 30) (b).

As observed in Figure 1b, 1-butene conversion decreases after two hours of reaction and then tends to a stable state with time on stream. The yields of C_8-C_{12} paraffins and C_8-C_{12} olefins are slightly reduced as 1-butene conversion decreases.

These results reveal the importance of the acidity of the zeolite in the oligomerisation-cracking reactions.

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CATALYTIC METHODS OF ENHANCED OIL RECOVERY RESERVOIRS OF OIL FIELDS

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World proven crude oil reserves are more 1,500 billion barrels according to OPEC experts [1]. The current state of development of many oilfields exploited in the world is characterized by a progressive decline in oil recovery and an increase in the unit cost per barrel of oil produced. The value of oil recovery does not exceed 25-40 % in the vast majority of the countries, and tends to decrease, while the proportion of heavy oil is growing. In Russia, 67 % of all oil producing fields are hard-to-recovery. This is due to the presence of a highly viscous oil (13 % of oil fields) and low permeability reservoirs (36 % of fields) [2].

The present paper discusses the possibilities of application of modern catalytic technologies for improving the efficiency of enhanced oil recovery and trends in catalytic research in this field. Experimental section is devote to the results of a study of the catalytic properties of inorganic matrices oil-bearing rocks with respect to the reaction ammonium nitrate decomposition, which is characterized by high level of gassing, and typical tests reaction of hydrocarbons (HC) oxidation – reaction of methane oxidation, and hydrocracking of asphaltenes as an example of the reaction of heavy HC transformation.

The basic scientific approach considered in this paper is based on the use of intrinsic catalytic properties of oil-bearing rocks' inorganic matrices for development effective catalysts for oil production and simultaneously upgrading of heavy oils in situ and creation of corresponding advanced technologies.

We propose to employ the intrinsic catalytic properties of the inorganic matrix of oil-bearing rocks in order to:

– synthesize in situ active catalytic systems;

– synthesize nanosized clusters of active components on natural inorganic matrices by injecting the precursors into the field;

– catalyze transformations of heavy oil hydrocarbon components.

Different natural inorganic matrices (basalts, clays, sandstones), which contain the heavy hydrocarbon compounds, have been studied in present paper. The fulfilled studies provided data on physicochemical and structural properties of matrix samples (chemical composition, specific surface area, pore volume), their catalytic activities to oxidation and hydrocracking of oil hydrocarbon components. The catalytic activities of oil-bearing rock matrices of various natures (basalts, clays, sandstones) with respect to decomposition of ammonium nitrate, oxidation of hydrocarbons and carbon monoxide were observed for the first time. The natural oil-bearing rocks under study were discovered to be more catalytic active to decomposition of ammonium nitrate than the industrial alumina-platinum catalyst. The characteristic features of basalt and clay matrices are considerable contents of transition and alkaline earth element oxides (2.75 – 3.3 wt % Fe; 0.3 – 0.4 wt % Ti; 7.2 – 1.4 wt % Mg) and large surface areas (25 – 15 m^2/g) that are sufficient for achieving catalytic reactions on the solid surface. Sandstone matrix samples are characterized by small surface areas, low contents of magnesium and iron, and the absence of manganese and cerium compounds that behave as promoters of catalytic activities to various catalytic systems. The differences in the chemical compositions and textures are the reasons for different catalytic activities of the matrices with respect both to transformations of oil hydrocarbon components (oxidation of methane and butane, hydrocracking of heavy oil components – asphaltenes), when the formation of active surface complexes is determining, and to liquid-phase decomposition of ammonium nitrate. The use of natural material matrices as catalyst supports (with catalytic systems Fe/basalt, Ni/basalt and Fe/clay as examples) for transformation of oil hydrocarbon components demonstrated that natural inorganic matrices are promising agents for in situ synthesis of active catalytic systems.

The obtained experimental data support the hypothesis about feasibility of catalytic reactions in oil beds using natural materials – oil-bearing rocks (sandstones, clays, basalts) – as catalysts and can be helpful for development of advanced technologies to enhance oil recovery. Possible methods of delivery catalytic systems in to the matrix and methods of activation them in oil reservoirs, allowing to create catalytic reactors in situ are also discussed in the paper.

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THE DEVELOPMENT OF THE PROCESS OF HYDROTHERMAL DECOMPOSITION OF CHLORIDE SOLUTIONS IN BATCH AND FLOW REACTORS

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Study the hydrolysis of metal chlorides is of particular interest in connection with the problems of materials science, geochemistry, general and technical chemistry and chemical engineering problems. In this study special attention special attention was paid to the development of effective methods of hydrothermal decomposition of aluminum chloride solutions to create innovative technology for hydro-chemical alumina production from kaolin raw material.

It was assumed consideration the simultaneous presence in the starting aluminum-chloride solutions of chloride impurities Fe, K, Na, Ca and Mg.

Hydrothermal synthesis of Al_2O_3, AlO(OH) and Fe_2O_3 were conducted using a batch type autoclave and flow reactor at temperatures from 453 to 483 K at a pressure of 1.6-2.3 MPa by decomposition process of aluminum-chloride solutions for 4-10 hours. The scheme of laboratory setup is shown in Figure 1.

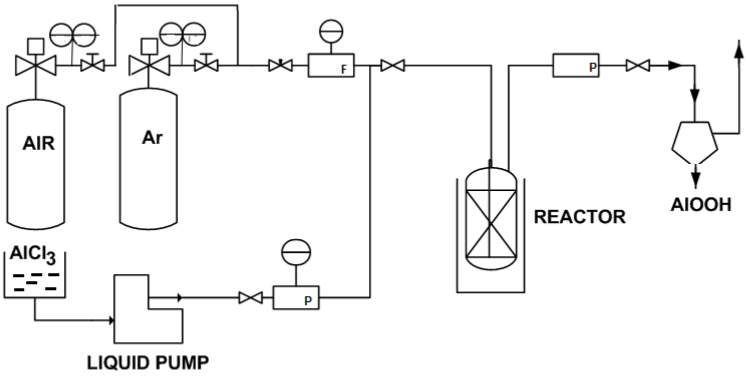

Figure 1. The scheme of laboratory setup with flow reactor

In present paper the original technique was developed for to move the balance of the following reversible reactions in the direction of formation of the reaction products, ie, right:

$$AlCl_3 + 3H_2O \leftrightarrow Al(OH)_3 + 3HCl\uparrow$$

$$FeCl_3 + 3H_2O \leftrightarrow Fe(OH)_3 + 3HCl\uparrow$$

Alumina products obtained with the hydrolyzate is evaporated to a volume of 8-10 ml at 253 K, cooled to room temperature, washing with distilled water followed by centrifugation.

The proposed method of hydrothermal decomposition of Me-chloride solutions solves the problem of completeness of hydrolysis of aluminum chloride and ferric chloride. The resulting hydrolysis products dried at 353 K for 5 h were identified as boehmite and hematite, respectively.

The study of influence of the process conditions such as pH values, temperature, ionic strength, the presence of coagulants and surfactants, and other components (additives) showed the possibility of process control deposition of metal hydroxides and controlling the formation of oxide materials of desired texture (Fig. 2).

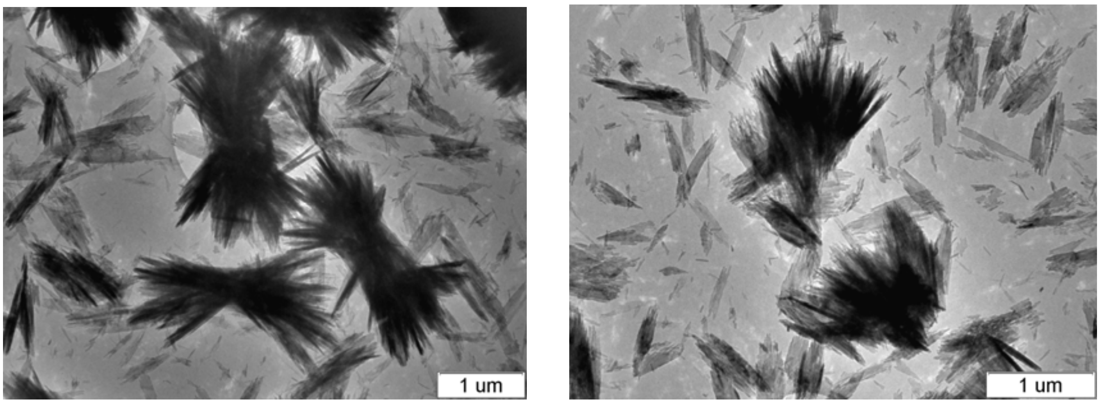

Figure 2. Transmission electron microscopy of high resolution data for boehmite

Thus, the possibility of hydrolysis of aluminum chloride under hydrothermal conditions the temperature range below 250 °C is shown experimentally.

2. Hydrothermal process for producing aluminum hydroxide provides:

a) processing of aluminum-chloride solutions with $AlCl_3$ content over a wide range from 11 to 21 %;

b) preparing at least 90 % of aluminum hydroxide from aluminum-chloride solution as a filterable precipitate;

c) the content of chloride ion in dried to constant weight aluminum hydroxide is not more than 4 %;

d) obtaining products with alumina predetermined morphology and texture.

Acknowledgement

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IMPROVING THE EFFICIENCY OF HIGH OCTANE GASOLINES MANUFACTURING

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For optimization of gasolines preparation processes (decrease in overexpenditure of expensive components), exact calculation of gasolines properties taking change of structure of raw materials and activity of catalysts into account is required. This problem is solved by the techniques developed on Department of Chemical Engineering and Chemical Cybernetics of Institute of Natural Resources of National research Tomsk Polytec University. These developments help to evaluate the detonation resistance of mix gasoline with high precision and to determine the optimal recipe of components mixing in order to obtain the desired product mark, taking the composition of raw materials and catalyst activity on previous stages of production (reforming, isomerization, catalytic cracking, alkylation) into account.

A computer modeling system compounding process is suitable for calculation of optimum recipes of high octane gasoline components mixing (Fig. 1).

Previously for determination of unadditive component of octane number binary interaction coefficients of mixture components were used [1]. However, experience has shown that without loss of accuracy we can use only nonadditivity of flow rates, which must be specified depending on the concentration of the main components. Thus, component flows composition is not require for accurate determination of the octane number, but only minor components concentrations.

$$OV = \sum_i OV_i \cdot w_i + \sum_i \sum_j OV_i \cdot OV_j \cdot w_i \cdot w_j \cdot B_i \cdot B_j ,$$

where

OV – octane number of mixture; OV_i, OV_j – octane number of i-th и j-th flow, respectively; w_i, w_j – concentration of i-th и j-th component in mixture, respectively; B_i, B_j – coefficients of i-th and j-th flows binary interaction.

This system is able to respond quickly in "online mode" to respond to changing composition of gasoline components and provide recommendations to change the recipe of gasoline preparation ensuring increase high-quality gasoline output and decrease of expensive components usage. The system can operate in "online mode" by connecting on the SOAP-protocol to a plant-wide database.

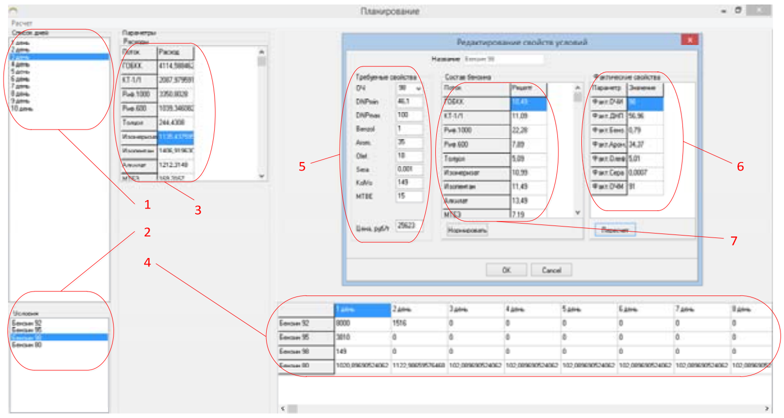

Figure 1. Dialog window of «Compounding» program

1 - List of days for calendar planning; 2 - Set of conditions for gasoline grades; 3 - Cost of components for each day; 4 - Table of calendar plan with calculated amount of produced grades of gasoline; 5 - Required properties of gasoline (octane number, vapor pressure, etc.); 6 - Actual properties of gasoline at given mixing formula; 7 - recipe of gasoline components mixing

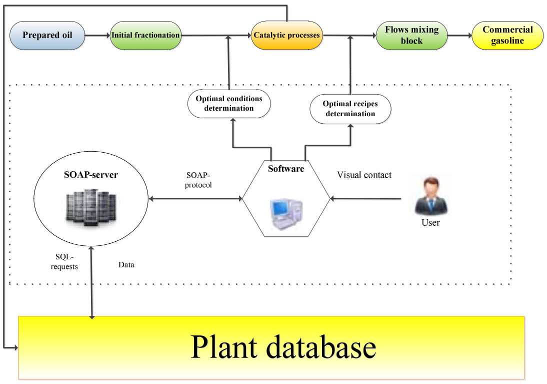

Figure 2. Scheme of developed software and plant-wide database interaction

General plant database receives a request to server at SOAP-protocol for user-defined parameters. In addition, the system will specify the schedule for production of various gasoline grades taking nonadditivity of octane number and saturated vapor pressure of mixing components based on PIMS program report and without it into account.

The economic efficiency of created software for operational and accurate calculation of flow rates may be more than 9 mil. Rub./year.(Table 1).

Table 1. Economic effect from optimization of flow rates

Gasoline brand	**Productivity, t/month.**	Extra profit, th. rub./year
Regular-92	188000	5640
Premium-95	91000	3060
Super-98	10000	500
In total	**289000**	**9200**

Refusal of traditional mixing recipes not taking changes in raw materials composition, catalyst activity during the high-octane gasoline components production and leading to increased use of high-quality and expensive flow into account, will lead to significant economic effect.

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PP-20

DEVELOPMENT OF MATHEMATICAL MODEL OF LINEAR ALKYLBENZENES SULPHONATION FILM REACTOR

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Linear alkilbenzenesulphonated (LABS) represent chemicals with a saturated hydrocarbonic chain from 10–13 atoms of carbon connected with one or sulfonate groups. These substances are one of the widespread anions used for production of synthetic detergents. Raw materials for production of LABS is an alkilbenzenesulphuric acid (ABSA) which is produced as a result of course of the following stages:

1) dehydrogenation of alkanes with receiving an alkenes on Pt-catalyst; 2) benzene alkylation by olefins with production linear alkylbenzene (LAB).3) sulphonation of LAB in a film reactor.

Earlier mathematical models of processes of dehydrogenation and alkylation were developed and successfully approved. The purpose of present work is development of mathematical model of process of LAB sulphonation process [1–6].

With application of methods of quantum chemistry calculations for definition of thermodynamic probability of target and side reactions were carried out.

The calculations showed that thermodynamic probability of sulphonation reactions in the double bond of side chain is higher than the probability of sulphonation reaction into the benzene ring, due to high reactivity of olefin radical. That is, an increased content of unsaturated LAB in the reaction mixture leads to intensification of side reactions.

According to this, the mathematical model of sulphonation process can be presented as follows:

$$\begin{cases} dC_{LAB}/dt = -W_1 - W_2 + W_{-2} - W_4 - W_5 - W_9 \\ dC_{ABSA}/dt = W_1 - W_2 + W_{-2} - 2W_3 + 2W_5 + 2W_6 \\ dC_{SO_3}/dt = -W_1 - W_3 - 2W_4 - W_7 \\ dC_{unsulph.prod.}/dt = W_2 - W_{-2} + W_7 \\ dC_{anhydrideABSA}/dt = W_3 - W_6 \\ dC_{PSA}/dt = W_4 - W_5 \\ dC_{H_2SO_4}/dt = W_3 \\ dC_{H_20}/dt = W_2 - W_{-2} + W_6 \\ dC_{LABuns}/dt = -W_7 \\ dC_{Ar}/dt = -W_8 \\ dC_{benzene}/dt = W_8 + W_9 \\ dC_{alkene}/dt = W_8 + W_9 - 4W_{10} \\ dC_{tetraline}/dt = 4W_{10} \end{cases}$$

$$\begin{aligned} W_1 &= k_1 \cdot C_{LAB} \cdot C_{SO_3} \\ W_2 &= k_2 \cdot C_{ABSA} \cdot C_{LAB} \\ W_{-2} &= k_{-2} \cdot C_{unsulph.product} \cdot C_{H_2O} \\ W_3 &= k_3 \cdot C_{ABSA}^2 \cdot C_{SO_3} \\ W_4 &= k_4 \cdot C_{LAB} \cdot C_{SO_3}^2 \\ W_5 &= k_5 \cdot C_{PSA} \cdot C_{LAB} \\ W_6 &= k_6 \cdot C_{anhydrideABSA} \cdot C_{H_2O} \\ W_7 &= k_7 \cdot C_{LABuns} \cdot C_{SO_3} \\ W_8 &= k_8 \cdot C_{Ar} \\ W_9 &= k_9 \cdot C_{LAB} \\ W_9 &= k_{10} \cdot C_{alkene}^4 \end{aligned}$$

The initial conditions: $t = 0$, $C = C_{0i}$, where – corresponding hydrocarbon.
ABSA – alkilbenzenesulphuric acid; PSA – pyrosulphuric acid; LABuns – LAB with unsaturated side chain; SK – the acid formed as a result of LABuns sulphonation in the side chain

Further researches are directed on development of mathematical model of sulphonation process connected with models of processes of dehydrogenation and alkylation that will allow to consider mutual influence of raw materials composition and technological modes for purpose of process optimization [7, 8].

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PROPYLENE GLYCOL OXIDATION OVER P-PROMOTED Ag/SiO_2 AND Fe/SiO_2 CATALYSTS: EXPERIMENTAL AND THEORETICAL COMPARISON

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Various organic compounds are known to be valuable products of propylene glycol (PG) oxidation, including methylglyoxal (MeGO), lactaldehyde, lactic and pyruvic acids, etc. [1-2] with MeGO being among the most important ones. Catalysts based on Pt, Au, Pd and their alloys containing various modifiers (e.g., Pb, Bi, Sn) were shown to be used in the process. Recently, an interest also arose to Ag- and Fe-based catalysts for liquid- and gas-phase PG oxidation [1-4]. Gas-phase MeGO production has several advantages compared to liquid-phase process, including higher selectivity towards MeGO. Bulk and supported Ag materials are traditional highly selective catalysts for alcohol oxidation, while iron phosphates look promising, since they possess mild acid-base properties, which facilitate their application as selective catalysts for alcohol oxidation reactions.

The aim of the present work was to carry out experimental and theoretical comparison of gas-phase PG oxidation over silica-supported P-promoted Ag- and Fe-based catalysts.

Real industrial diol oxidation catalyst represented by silver clusters (5 % mass. of Ag, particle size of 5-50 nm) immobilized in silicate-phosphate matrix was prepared according to [5,6]. $FePO_4/SiO_2$ catalyst (5 % mass. of $FePO_4$) was prepared using incipient wetness impregnation of SiO_2 by $Fe(NO_3)_3$ solution followed by step-by-step precipitation of iron salt by concentrated solution of ammonia orthophosphate, evaporation of solution at 80 °C, drying at 110 °C during 24 h and thermal treatment at 600 °C during 8 h.

Phase composition, textural properties, thermal stability of catalyst samples were studied using a complex of physical-chemical methods, including XRD, FTIRS, TGA, H_2-TPR and TPO. Catalytic tests were carried out using flow fixed-bed catalytic unit in the temperature range from 200 to 500 °C. Contact time was changed from 0.06 to 0.33 sec. Catalyst sample was placed into quartz tube reactor, bed height varied from 0.5 to 3 cm. Reaction mixture was passed through catalyst bed with weight hour space velocity of 1.5 l/min. Chromatographic analysis of products was carried out using “Crystal 5000.1” gas chromatograph (Chromatek, Russia) and Agilent 1200 HPLC chromatograph.

A theoretical interpretation of the mechanism of gas phase PG oxidation to MeGO over Ag and Fe catalysts was developed using Gaussian’09 program package installed at SKIF “Cyberia” supercomputer of Tomsk State University. Due to complexity of real catalysts, the developed cluster models were limited to metal and polyphosphate promoter, and their interactions with process adsorbates and/or intermediates was proposed. Geometry of all the obtained structures was fully optimized. In all cases the nature of stationary point was checked by vibrational frequency calculations. The majority of the optimized structures was in global energy minima and had real frequencies only. The absence of imaginary vibrational frequencies confirmed the stationary character of structures. When the structure had imaginary frequencies, IRC calculations were carried out to determine the transition state. The thermodynamic parameters of the molecules calculated were corrected for zero-point vibrational energy (ZPVE) and reduced to normal conditions (298.15 K, 1 atm) using thermal corrections to enthalpy and free energy. The parameters were also calculated for real process conditions.

Main process routes comprising partial oxidation of PG to aldehydes (MeGO, lactaldehyde, acetaldehyde, formaldehyde, etc.) as well as total oxidation routes were considered, and the corresponding reaction profiles were represented and compared for both catalysts under consideration. The main structural and energetic parameters for the key reaction adsorbates and intermediates as well as thermochemical data for their main transformations were predicted. Comparison of catalyst performance in PG oxidation was carried out, and process peculiarities were discussed. The results obtained can be used in further modeling of both gas- and liquid-phase PG oxidation over Ag- and Fe-based catalysts.

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INTEGRATED MEMBRANE REACTOR FOR ULTRAPURE HYDROGEN PRODUCTION BY REFORMING PROCESSES OF RENEWABLE RESOURCES AND SYNTHETIC FUEL

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Original integrated membrane reactor (IMR) for ultrapure (99,9995 %) hydrogen production by dry and steam reforming processes of renewable resources (methane, ethanol, fermentation products) and synthetic fuel (dimethyl ether – DME) is presented in this work. The IMR is a single unit device consisted of Ni(Al)-Co-based porous ceramic catalytic converter, prepared by self-propagating high temperature synthesis (SHS), and hydrogen selective 94 % Pd – 6 % Ru membrane.

It was shown that solid converters are much more active than granulated what can be explained by more intensive mass and heat transfer due to forced diffusion of substrates through a solid porous material. Among studied samples a non-additive effect was found on a reduced converter with composition 45 % Ni (5 % Al) – 50 % Co_3O_4 [1]. Using it 75000 $l/h \cdot dm^3$ of syngas in dry reforming of methane (DRM) at 800^{o}C was obtained. It is around 2.5 times higher than the values for other converters. Exhaustive conversions of ethanol and fermentation products were reached at 400^{o}C on the same sample [2]. A sequence of reactions in dry reforming processes of methane and ethanol was established by thermogravimetric analysis (TGA). The structure of converter was studied by BET, XRD, SEM, TEM, EDX and XAFS methods [3].

It was demonstrated that using the IMR in DRM selective hydrogen removal from reaction zone allowed to increase methane conversion up to 15 % in comparison with equilibrium value. Feeding the substrate at a rate of 9 L/h and T = 550 °C hydrogen productivity was 3.7 L/h, including 50 % of ultrapure hydrogen.

It was found that in DRE selective removal of ultrapure hydrogen decreased methane containing in products and increased the total yield of hydrogen. It was determined that feeding the substrate at a rate of 30 L/h and T = 600 °C hydrogen productivity was 9 L/h, including 1.6 L/h of ultrapure hydrogen.

Steam reforming of DME in the membrane reactor might be also a suitable approach for hydrogen production. At 450 °C and H_2O/DME = 4.5 there is 100 % conversion of DME with H_2/CO ratio ~19. In this case ultrapure hydrogen separation on Pd-based membrane is a possibility to use IMR to supply fuel cells [4].

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AQUEOUS PHASE REFORMING OF BIODERIVED HEMICELLULOSIC OXYGENATES

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During Aqueous phase reforming (APR) offers an attractive option as a conversion platform for a wide spectrum of biomass-derived feedstocks to energy fuels. APR is a catalytically-driven process that has been demonstrated to effectively produce hydrogen and liquid fuels from bioderived substrates such as polyols [1] and cellulose [2] under hot compressed water. While APR could be even extended in principle to utilize other biomass of commercial importance, the APR of hemicellulosic oxygenates – xylose and xylitol – has received little attention despite the tremendous opportunities it presents for the full utilization of second generation (2G) biomass feedstocks. Thus, in this work, we investigated the APR of xylose and xylitol for hydrogen production, which could be used for fuel cell applications. The work investigated Pt/Al_2O_3 catalyzed APR of aqueous solutions of xylose and xylitol in a batch reactor. Feed is prepared as 1 % w/w solution, 100 ml of which is charged into the reaction vessel along with Pt/Al_2O_3 catalyst. The reactor is heated to 225 °C for a set period of time, after which the reactor is the quenched to room temperature and the gas and liquid products collected and analyzed via chromatographic techniques. Figure 1 shows the conversion and H_2 yield for the APR of xylose and xylitol at different reaction times. Hydrogen yields after 7 hours of xylitol APR reached 22 % of the theoretical at 87 % conversion. All throughout the reaction, H_2 yields for xylitol APR are 2.5 times higher than that of xylose APR, despite the apparent reactivity of the latter (almost complete conversion for xylose). This difference in hydrogen yields points to different reaction pathways that influences the evolution of H_2 via APR.

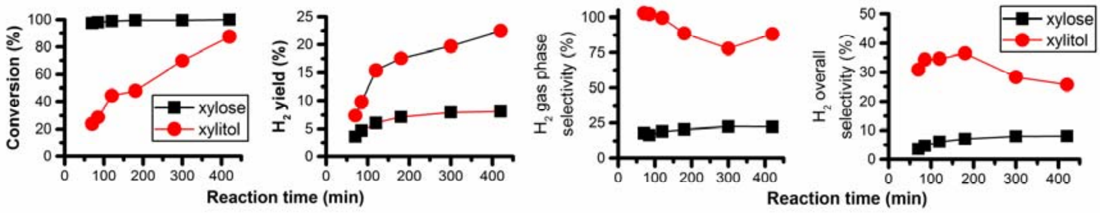

Fig. 1. Conversion, H_2 yield, H_2 selectivity (gas-phase and overall) curves for APR of xylose and xylitol

H_2 selectivity values provide additional insights into the APR of hemicellulosic oxygenates. While complete APR of xylose (a C_5 aldose) and xylitol (a C_5 alditol derived from hydrogenation of xylose) proceeds according to the following overall stoichiometry.

$$\text{Xylose: } C_5H_{10}O_5 + 5H_2O \rightarrow 5CO_2 + 10H_2 \quad (1)$$

$$\text{Xylitol: } C_5H_{12}O_5 + 5H_2O \rightarrow 5CO_2 + 11H_2 \quad (2)$$

Numerous catalyst surface and solution phase side reactions act as hydrogen sinks. Thus, in calculating H_2 selectivity values, one may use a *gas-phase* selectivity [1] and an *overall* selectivity [3], which takes into account gas-phase and solution-phase side reactions, respectively. Relatively high gas-phase selectivity in the APR of xylitol (>75 %) suggests that reforming reactions predominate over other catalyst-mediated gas producing reactions. This is in contrast with the low gas-phase selectivity values for the APR of xylose, which shows increased alkane producing side reactions. Overall selectivity values are relatively low for xylitol, and even lower for xylose. This implies significant participation of solution-phase chemistry producing liquid-phase intermediates with lower activity towards APR. The trends in reactivity and H_2 selectivity may be attributed to the inherent chemistry of xylose and xylitol. Xylose has carbonyl functionality that renders it more reactive towards solution-phase chemistries. One can surmise that early reactions in xylose APR is dominated by solution phase reactions. On the other hand, xylitol requires initial activation via dehydrogenation of any of its hydroxyl groups before any solution phase reactions may ensue.

Table 1. Composition of gas products of the APR of xylose and xylitol (reaction time = 1 hour)

Component	Composition, mol%	
	Xylose	Xylitol
H_2	32.7 %	71.8 %
CO_2	49.4 %	22.4 %
CO	2.7 %	0.1 %
Alkanes	15.3 %	5.7 %
CH_4	2.5 %	3.3 %
C_2H_6	1.2 %	1.3 %
C_3H_8	11.7 %	1.1 %

Thus, Hydrogen production via aqueous phase reforming is successfully demonstrated using hemicellulosic oxygenates xylose and xylitol as substrates. Xylitol exhibits better APR characteristics, in terms of H_2 yields and selectivities over its dehydrogenated counterpart xylose. Suppressing xylose reactivity via in-situ hydrogenation using tandem hydrogenation-reforming reactors would be an excellent approach to enhance hydrogen production from xylose.

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STUDY ON MESOPOROUS-SUPPORTED CATALYSTS FOR SIMULTANEOUS CO_2 AND STEAM REFORMING OF BIOGAS

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The methane-CO_2 reforming to produce syngas is a very attractive route to produce energy and valuable compounds. This reaction offers advantages over methane steam reforming to produce a H_2/CO ratio of about 2, adequate for processes such as the production of higher hydrocarbons and derivatives [1]. CO_2 reforming of methane with a feed gas containing steam has been suggested to reduce carbon deposition. Moreover, in the presence of steam, methane steam-reforming occurs simultaneously and thereby higher selectivity for both CO and H_2 can be achieved, and also the H_2/CO ratio of the product gas can be controlled [2,3].

Recently, the most widely used catalysts for CO_2 steam reforming reaction are based on Ni and noble metals, much more resistant to carbon deposition than Ni catalysts, but generally more expensive. Moreover, the silica SBA-15, which possesses larger pores and higher thermal stability, may be used as a promising catalyst support [4].

In the present study, 10 % Ni/SBA-15 and 0.5 % Rh/SBA-15 catalysts were prepared, and their performances over the reaction of combined carbon dioxide and steam reforming of methane were investigated.

Ordered mesoporous silica SBA-15 was synthesized in a spherical shape, according to the procedures [5] and used as catalyst carrier. The supported Rh and Ni catalysts were prepared with the Incipient Wetness Impregnation (IWI) method. The phase structures of the samples were characterized by XRD, CO_2-TPD, BET and FESEM analyses. In order to verify real amount of deposed metal, ICP-MS apparatus was used. The activity of the prepared catalysts was analyzed in a fixed-bed reactor, feeding a gas mixture, composed by CO_2, CH_4 and steam ($CO_2/CH_4 > 0.75 \div 1.5$, $H_2O/CH_4 \cong 1.5$). The gas hourly space velocity (GHSV) through the catalytic bed was varied. Before each activity test, catalyst was reduced in H_2 at 500 °C for 30 minutes.

The first tests was carried out on both Ni and Rh supported catalysts at GHSV = 26000 h^{-1} and with CO_2/CH_4 ratio equal to 0.85. Results in terms of CH_4 conversion, H_2 yield and H_2/CO ratio are shown in Fig. 1.

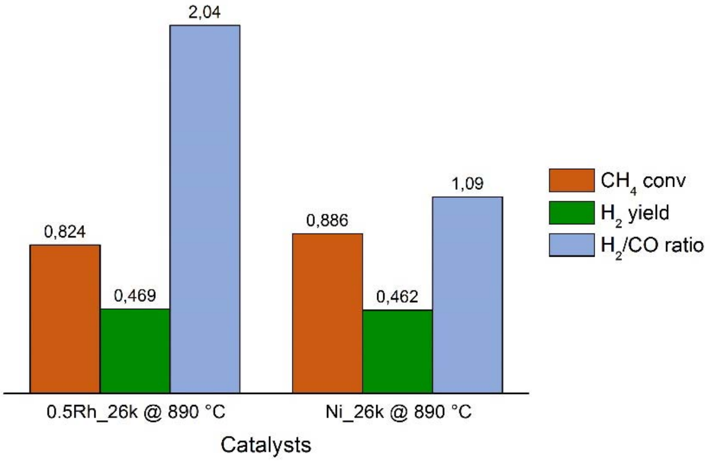

Figure 1. Comparison between Rh/SBA15 and Ni/SBA15 at GHSV=26000 h^{-1} and CO_2/CH_4=0.85

The two catalysts reached similar methane conversion and H_2 amount produced was about comparable. Otherwise, H_2/CO ratio doubled with Rh based catalyst, meaning higher selectivity toward H_2 production. In particular, with 0.5 %Rh/SBA15 catalyst H_2/CO ratio was equal to 2, required value for the methanol synthesis [6].

Deeper studies were performed on Rh/SBA15 catalyst by varying space velocity. Activity test at GHSV equal to 44000 and 15000 h^{-1} were carried out and performances were compared with those obtained at GHSV = 26000 h^{-1}. As expected, CH_4 conversion and H_2 yield decreased by increasing space velocity, but H_2/CO ratio was maintained about 2.

In conclusion, SBA15 supported 0.5 wt % Rh was proved to be a promising catalyst over the reaction of combined carbon dioxide and steam reforming of methane.

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PP-25

CATALYTIC SYNTHESIS OF 1,3-DIARYL-2-PROPENE-1-ONES BY USING HETEROPOLYACIDS AS HETEROGENEOUS RECYCLABLE GREEN CATALYSTS

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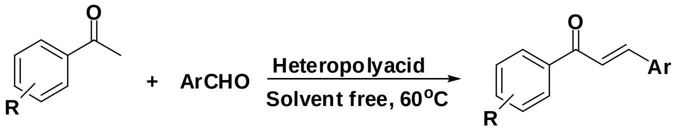
(1,3-diaryl-2-propene-1-ones), chalcones are natural substances found in a number of plants or are synthetically prepared. They display many biological activities, *viz*., antiviral, anti-inflammatory, antimicrobial, antimitotic, antitumor, analgesic, and antipyretic properties [1]. In addition, these compounds are of a high interest due to their use as starting materials in the synthesis of a series of heterocyclic compounds [2] like, isoxazoles, quinolinones, thiadiazines, benzofuranones, benzodiazepine, tetrahydro-2-chromens [3], flavones, etc. We have demonstrated an alternative simple procedure for the synthesis of 1,3-diaryl-2-propene-1-one derivatives using Wells–Dawson, $H_6[P_2W_{18}O_{62}]$ heteropolyacid catalyst as an ecofriendly, reusable, inexpensive and efficient catalyst. The method has advantages in terms of yield, heterogeneous nature, expenses, availability of reagents and reusability of the green catalyst, short reaction times and easy work-up procedure.



1a-j **2a-j** **3a-j**

Scheme 1. Synthesis of 1,3-diaryl-2-propene-1-ones using heteropolyacid catalysts at water as a green solvent

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PP-26

SYNTHESIS OF β–AMINO CARBONYL COMPOUNDS USING ZnO NANOPARTICLES AS A GREEN, EFFECTIVE AND REUSABLE CATALYST

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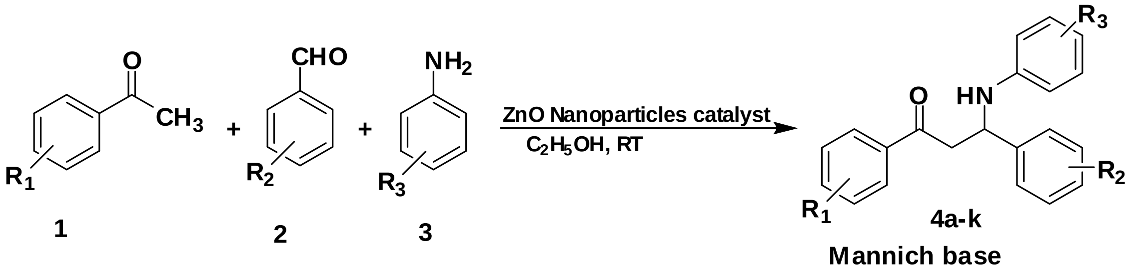
Cysteine proteases are ubiquitous in nature and have been implicated in the etiology of a number of disease states [1]. Over the past two decades, selective and reversible inhibitors for this class of enzymes have been an area of intense research [2]. These investigations have led to a number of reversible inhibitors such as peptidyl aldehydes, α-ketoamides and α-keto heterocycles [3]. A new efficient one-pot three-component condensation of aromatic aldehydes, aromatic ketones, and aromatic amines in the presence of ZnO nanoparticles as an inexpensive and effective catalyst for the synthesis of β-amino carbonyl compounds by Mannich reaction is described. The reaction was carried out at room temperature under solvent-free conditions. Mild reaction temperature, cost-effective catalyst, simple product separation and catalyst recycling were notable achievements in the reaction. Simple experimental conditions and product isolation procedure make this protocol potentially applicable for the development of a clean and environment-friendly strategy for the synthesis of β-amino ketones. The present methodology offers several advantages such as good yields, short reaction times and a recyclable catalyst with a very easy work-up. In order to evaluate the catalytic efficiency of ZnO nanoparticles, a model reaction was carried out on the synthesis of Mannich base **4a** by condensation of acetophenone, benzaldehyde and aniline (Scheme 1).



Scheme 1. Synthesis of β-amino carbonyl compounds from amines, acetophenone and aldehydes catalyzed by ZnO nanoparticles catalyst

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HYDROGEN GENERATION VIA PHOTOCATALYTIC WATER SPLITTING USING A MESOPOROUS TiO_2 DOPED WITH PLATINUM

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Mesoporous TiO_2 semiconductors were synthesized by a sol-gel technique, using a triblock-copolymer-templating, named Pluronic F127. Pt was added by different percentages (i.e. 1.00 wt %, 2.50 wt %), followed by calcination at 500 °C and 550 °C. Water splitting performance under near UV light for hydrogen production was studied in the Photo-CREC-Water II reactor using ethanol at 2 % v/v as an organic scavenger. The present study shows that TiO_2 with 2.50 wt % of Pt loading displays high photocatalytic activity towards hydrogen. Evaluated Quantum Yields (QY) reached 27 %.

Introduction

Hydrogen is a clean energy vector of great importance for the world's sustainable future development [1]. Water splitting using solar energy is one of the most attractive approaches to produce hydrogen.

Photocatalyst Characterization

The 2.50 wt % Pt/TiO_2-Meso-550 °C of this study showed: a) rutile and anatase phases with XRD, b) reduced band gap at 2.34 eV employing UV-vis spectroscopy and a Tauc plot, c) 10 nm TiO_2 particles with SEM-EDX, d) 140 m^2/g BET surface area and a 10 nm and 20 nm bimodal pore size distribution.

Photocatalytic Performance

The photocatalytic activity of the semiconductors was carried out using a bench scale Photo-CREC-Water II (PCWII) photoreactor.The PCWII consisted of a 2.65 L internally irradiated slurry annular reactor (total volume of slurry, 6.0 l) with a 15 W T8 Black-Light-Blue (F15T8/BLB) lamp. The photocatalyst loading was 0.15 g L^{-1} in an acid medium (pH = 4.0) and the volume of the reaction mixture was 6.0 L. Ethanol was used as a renewable organic scavenger at 2 % v/v accordingly with our previous work [2].

Figure 1 reports the significantly improved hydrogen production of the 2.50 wt % Pt/TiO_2-Meso-550 °C photocatalyst: 3 times enhanced performance versus other photocatalysts of the present study. Calculations based on these data yielded a 0.27 QY. This QY is among the highest reported in the technical literature.

Table 1. Physicochemical properties of mesoporous TiO_2, Pt-TiO_2 and Degussa P25

Photocatalyst	QY (%)	Band Gap(eV)
2.50 wt % Pt/TiO_2-Meso-550 °C	2.34	27
2.50 wt % Pt/TiO_2-Meso-500 °C	2.44	26
1.00 wt % Pt/TiO_2-Meso-550 °C	2.59	16
1.00 wt % Pt/TiO_2-Meso-500 °C	2.62	15
TiO_2- Meso-550 °C	2.99	9
TiO_2- Meso-500 °C	2.96	7
1.00 wt % Pt-Degussa P25	2.73	7
Degussa P25	3.10	1

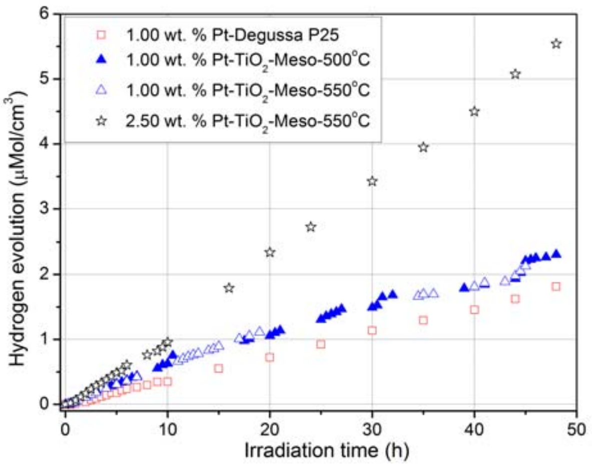

Figure 1. H_2 evolutions for different photocatalysts at pH = 4, EtOH 2 % v/v.

Table 1 shows the physicochemical properties of mesoporous TiO_2 and Pt-TiO_2 with different Pt loadings. Table 1 also reports their Quatum Yields/Photonic Efficiencies.

Figure 1 reports a steady hydrogen increase throughout the entire experiment with no observable activity decay. Experiments in the Photo-CREC Water II reactor show a significant increase in hydrogen production with Pt addition in the 2.50 wt % Pt/TiO_2-Meso-550 °C.

Conclusions

a) Pt can be incorporated in mesoporous TiO_2 framework during sol-gel synthesis.
b) Pt-mesoporous TiO_2 displays valuable photocatalytic activity for hydrogen generation via water splitting.
c) Pt-TiO_2 shows promising QYs of 27 % for the 2.50 wt % Pt/TiO_2-Meso-550 °C.

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EXPERIMENTAL STUDY AND CFD-PBM SIMULATIONS OF A BUBBLE COLUMN WITH DIFFERENT LIQUID PROPERTIES

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Bubble column reactors have been widely used in chemical industrial processes because of its advantages of good temperature control, simple construction, large capacity and low cost [1,2]. The liquid properties play important roles in the hydrodynamics and bubble coalescence and breakup in a bubble column [3].

In this work, the effect of liquid viscosity on the total gas holdup and gas holdup structure was studied with glycerol solutions of different viscosities, as shown in Figure 1. In the low viscosity range, the liquid viscosity had a less effect on the bubble behaviors. In the high viscosity range, however, increasing liquid viscosity significantly decreased the total gas holdup and the volume fraction of small bubbles. The CFD-PBM coupled model successfully predicted the effect of liquid viscosity on the total gas holdup and volume fractions of small and large bubbles in both the homogeneous and heterogeneous regimes.

The effect of surface tension was studied with pure liquids of different surface tensions and alcohol solutions varying in concentration. For the pure liquids, the total gas holdup increased with decreasing liquid surface tension. The CFD-PBM coupled model could also predict the effect of liquid surface tension on the total gas holdup, as shown in Figure 2. The coalescence of small bubbles were inhibited more significantly in alcohol solutions than in pure liquids and the effect of alcohol was studied in the whole concentration range. The critical ethanol volumetric concentration, where the gas holdup reached its maximum, was about 3 %. The results showed that the dynamic surface tension effect [4] was the critical factor affecting the bubble behaviors in the ethanol solutions.

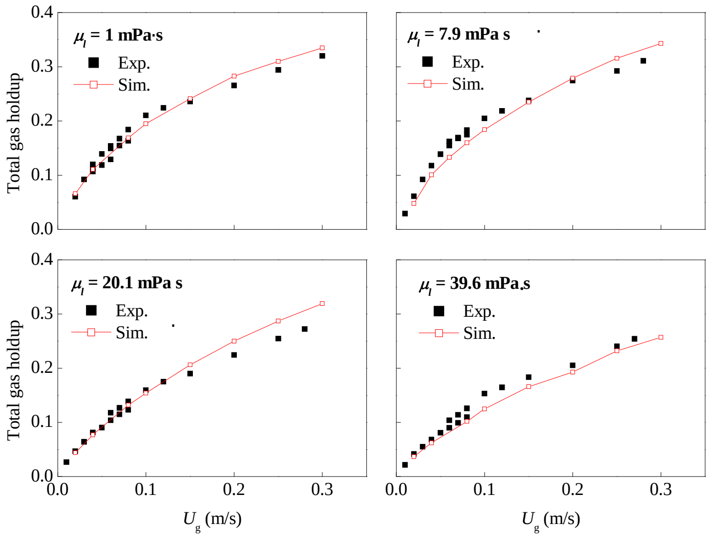

Figure 1. Effect of liquid viscosity on the total gas holdup at different gas superficial velocities

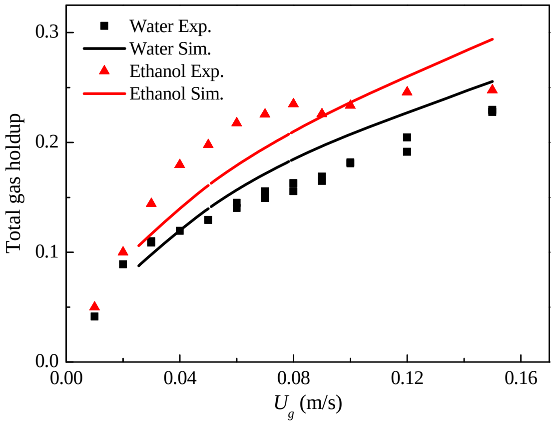

Figure 2. Effect of liquid surface tension on total gas holdup in water (σ_l = 0.0727 mN/m) and in ethanol (σ_l = 0.0223 mN/m)

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SYNTHESIS OF FRAGRANCE COMPOUNDS FROM BIORENEWABLES: HYDROFORMYLATION OF TERPENES

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Terpenes are abundant renewable feedstock for the flavor and fragrance industry [1,2]. Major terpene sources are essential oils and natural resins as well as by-products of the citric juice production and paper production industries. Since many natural aroma compounds contain in their structure an aldehyde group, the hydroformylation of terpenes has attracted a special attention as a convenient method to obtain aldehydes and compounds derived from aldehydes with interesting organoleptic properties [3]. The hydroformylation of the most abundant terpenes, such as limonene, β-pinene and camphene, was quite extensively studied; however, the works using functionalized monoterpenes (for example, linalool and nerolidol) and sesquiterpenes as the substrates in hydroformylation reactions are really scarce. Within the project aiming the valorization of natural ingredients of essential oils, we have been interested for several years in the catalytic transformations of terpenes, including their hydrofomylation [4-6]. In the present communication, we will focus on our recent results on the hydroformylation of terpenes, in particular, sesquiterpenes such as caryophyllene and its derivatives.

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PP-30

MODIFIED ZSM-5 ZEOLITE IN THE CONVERSION OF FURFURYL ALCOHOL TO LEVULINIC ACID

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Introduction

The route to synthesize LA from FA is the hydratation and ring opening of FA [1-4]. The synthesis of levulinic acid (LA) from furfuryl alcohol (FA) has been studied since the mid-twentieth century, and the majority of studies have been patented by various authors [1-4]. Usually, the FA hydratation to LA takes place using homogeneous strong acid catalysts as sulphuric or hydrochloric acids [2, 4]. The disadvantages of using homogeneous acid catalysts are well known: risk in handling, high toxicity, the need of special infrastructures for their use with the corresponding associated cost, high amounts of catalyst, and the difficulty of their separation and recovery. Therefore, promising studies about this reaction has been included using heterogeneous catalysts with adequate acidity and textural properties [3], that is why his work is focused on the study of the production of LA from FA using different heterogeneous acids catalysts as substitute of hydrochloric acid. Even more, a water soluble aliphatic ketone was added to the reaction media in order to obtain a higher efficiency in the production of LA. [2].

Materials and Methods

Test of activities were carried out in the semi-continuous batch reactor using ZSM-5 zeolites with different SiO_2/Al_2O_3 ratio (SiO_2/Al_2O_3:50 and SiO_2/Al_2O_3:23). The ZSM-5 zeolites were purchased from Zeolyst International (ammonia form). These were calcined at 823 K to their protonated forms H-Z (50) and H-Z (23). The H-ZD (50) and H-ZD (23) are the zeolite H-Z (50) which was subjected to desilication process using extraction of silica in a solution of NaOH (0.2 M). After the optimization of the operating conditions, the activities test were carried out using 0.5 g of catalyst at 413 K and 20 bar of H_2 pressure using as co-solver methyl ethyl ketone (MEK).

Results and Discussion

In Figure 1 are shown the yields to LA and FA conversions with the above reference catalysts. The results show that zeolite H-ZD (23) has the highest LA yield respect the other zeolites tested. This H-ZD (23) zeolite present an increased up to 18 percentage with respect to the parent H-Z (23), indicating the effectiveness of the desilication process, which is highly related with increased in its mesopority and acidity (Table 1). However the results are not positives for H-ZD (50), because the LA yield decreased when it compared with its protonated form (H-D (50). Due to the good activity result of the H-ZD (23) zeolite, this catalyst was recycled (H-ZDR (23)) to check its stability. Only a little difference was observed between both zeolites. The LA yield obtained with H-ZDR (23) reaches a 74 % after 23 time on stream, showing a similar behavior than H-ZD (23). The slight difference in the LA yield can be related with the variations in some surface properties summarized in Table 1. The H-ZDR (23) has a slightly decrease of mesoporosity, which includes a little decrease of mesopore area and pore diameter, and greater loss of activity. Nonetheless, the viability of recovery and recycling of the H-ZD (23) zeolite is highly positive, because the yield only decreased up to 7 mol %, which is a factor very important related with the economical feasibility. In addition, it is demonstrated that the used of heterogeneous catalyst is possible in this process, reaching a high LA yield as when it is used homogeneous catalysts, avoiding the homogeneous catalysts problems.

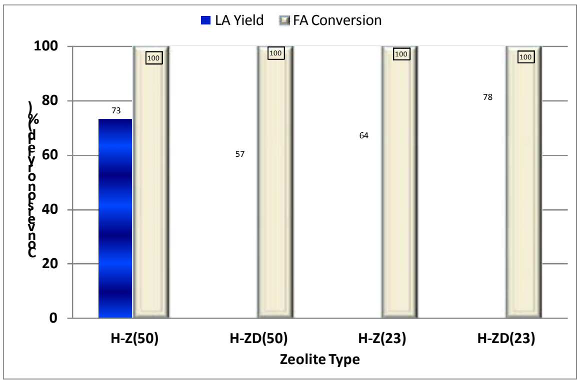

Figure 1. Yield to LA using different zeolites. Operation conditions: 413 K, 10 bar of H_2, 0.5 g of catalyst, 36 vol % of FA in MEK

Catalyst	Type of acidity (mmol NH_3/g)		Total acidity (mmol NH_3/g)	S_{BET} (m^2/g)
	Bpy	Lpy		
H-Z(50)	0.463	0.363	0.826	395
H-ZD(50)	0.207	0.454	0.661	407
H-Z(23)	0.144	0.8	0.944	314
H-ZD(23)	0.194	1.012	1.206	322
H-ZDR(23)	0.063	0.875	0.938	332

Table 1. Acidity and S_{BET} of the different zeolites. Lpy: pyridine coordinative bonded on lewis acid sites, Bpy: Brönsted acid sites

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Acknowledgements

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PP-31

THE ABSORBENTS FOR THE SULFUR REMOVAL REACTOR STABLE OPERATION

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Virtually, all of the hydrocarbon feedstock subjected to catalytic processing in the production of synthesis gas must first be purified of sulfur compounds. Various kinds of renewable raw materials, primarily biogas, have appeared during recent years in addition to mineral raw materials (natural, casing-head and refinery gases).

Biogas can be exploited directly as a fuel (including fuel cells) or as a raw material for the production of syngas and/or hydrogen. Depending on its source (i.e., landfills, anaerobic digestion plants), it can also contain significant quantities of undesirable contaminant compounds, including hydrogen sulphide (H_2S) and organosulfur compounds. Therefore, it is important to include biogas purification steps before its target use.

Main sulfur absorbent properties ensuring sulfur removal reactor stable operation are its sulphur absorption capacity and mechanical strength. As for the first, the experience of sulfur absorbents industrial use shows that the superfine particles of the absorbent (now mainly doped ZnO) can sinter resulting in the sulfur capacity loss [1, 2]. The results of 6000 hour-long runs of stabilized and non-stabilized ZnO-based absorbents in a pilot unit under industrial conditions and their extrapolation demonstrate a drastic decrease of sulphur capacity for the non-stabilized absorbent and appreciable even for the stabilized one. Of course, 5-8 wt % of stabilizing component slightly decrease total ZnO content and, proportionally, the start sulphur capacity. However, if stabilized absorbent sulphur capacity will decrease twice in 5-6 years, then that of nonstabilized one – in two years.

So stabilization is a good reserve of sulphur absorbent quality, especially if sulfur content in the feedstock is low so the loading runs some years.

The mechanical strength plays its role (in the case of ZnO-based materials) mainly during absorbent shipment and loading, as the mechanical strength of the sulfurized ZnO absorbent is sufficiently higher than initially.

To analyze the effect of stabilizing component, the following samples were studied:

1. The superfine ZnO powder used for the manufacturing of sulfur absorbents extrudates and tablets.

2. The extrudates (5 mm in diameter) of superfine ZnO, containing 6 % of MgO.

3. The extrudates (5 mm in diameter) of superfine ZnO, containing 3 % of the superfine graphite powder.

4. The tablets (6.1 diameter, 4.5 mm in height) composed as the sample 3.

The samples were calcined at 650 °C during various time intervals. The calcination temperature used provided the noticeable recrystallization for not more than 10 hours. Then the crystallites sizes were determined using X-ray powder diffraction technique.

The samples recrystallization characteristic times were then estimated (see the table).

Sample	1	2	3	4
Recrystallization characteristic time at 650 °C, hours	8.9	8.4	5.9	5.3

Thus there are two groups of samples concerning recrystallization times: (1, 2) and (3, 4). In the first one, the recrystallization occurs noticeably more slowly.

Conclusions

1. Recrystallization occurs both by particles sintering in their tight contact points and by crystallites coalescence (as their boundaries move) because for the powders (where there are no tight contacts) recrystallization times are about one and a half times greater than those for granules of the samples 3 and 4.

2. MgO in the sample 2 blocks particles sintering without affecting the crystallites coalescence, because this sample recrystallization time is close to that of ZnO powder (sample 1) and not to those of similar (excluding mechanical strength) extrudates of the sample 3.

3. Apparently, MgO is located in particles contact points, ensuring both extrudates mechanical strength and stability of absorbent sulphur capacity.

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PP-32

RESEARCH ON INFLUENCE OF ALKYLAROMATIC HYDROCARBONS ON EFFICIENCY OF LINEAR ALKYLBENZENES SYNTHESIS REACTOR PROCESSES

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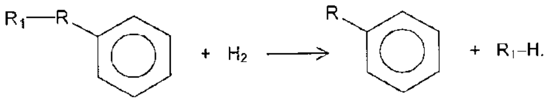
The technology of multistage complex production has to provide maintenance of a high exit of target products at preservation of the demanded quality and minimization of waste (sub-standard lots of products with the high maintenance of by-products). Creation of such technology is possible only on condition of increase of efficiency of each of the interfaced reactor processes of all stages taking into account their interrelation by method of mathematical modeling. The main indicators of ABSA quality at LAB sulphonation stage are: content of ABSA (not less than 96 % mas.); content of sulfuric acid (no more than 2 %); content of unsulphonated substance (no more than 2 %) [1].

The executed researches showed that contents of alkylaromatic hydrocarbons in raw materials of dehydrogenation process affects significantly indicators of closing stage – the film sulphonation reactor.

Alkylaromatic connections can be split both at dehydrogenation and sulphonation stage with formation of light unsaturated hydrocarbons and alkylaromatic compounds with one methyl radical.



As sulphonation stage reaction procces occurs in thin film, and necessary condition of qualitative ABSA receiving is distribution of LAB on reactionary surface of cylinders.

In different zones of reactionary surface of cylinders there can be as unsulphonation of LAB and its extra sulphonation with formation of polymeric compounds. The reaction network of sulphonation process is presented in figure 1.

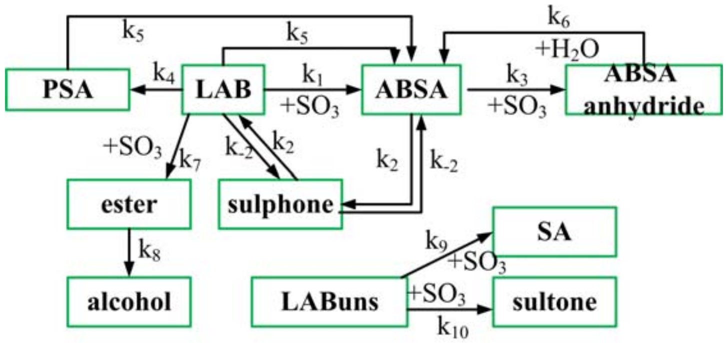


Figure 1. Reaction networks of hydrocarbons in sulphonation process

In figure 2 and 3 dependence of ABSA content and viscosity on SO_3/LAB molar ratio of presented.

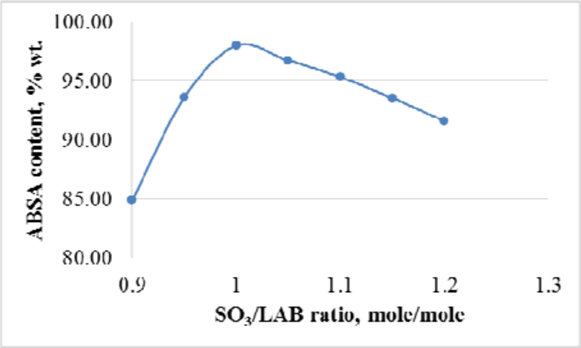


Figure 2. Dependence of ABSA content on SO_3/LAB molar ratio

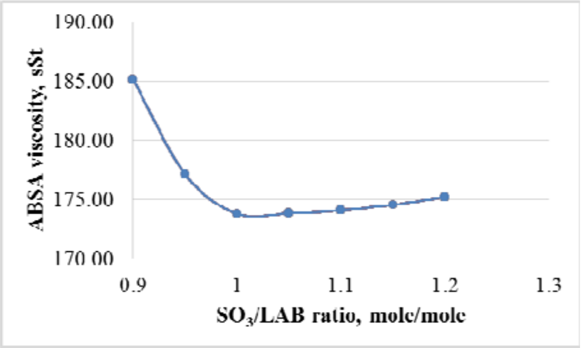


Figure 3. Dependence of ABSA viscosity on SO_3/LAB molar ratio

The received dependences allow to regulate SO_3/LAB ratio at the set amount of aromatics in raw materials of dehydrogenation reactor for the purpose of required ABSK content maintenance.

The increase in concentration of aromatic hydrocarbons in raw materials of dehydrogenation process, first of all, promotes increase in concentration of high-viscosity components (homologs of indan, tetralin – alkylation process by-products) which at a sulphonation stage negatively affect viscosity of mixture, reducing intensity of target reactions.

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ONE-REACTOR SCHEME FOR NO AND N_2O LOW TEMPERATURE ABATEMENT FROM TAIL GAS IN NITRIC ACID PRODUCTION

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Nitric acid production is one of the major sources of NO and N_2O in the chemical industry. To reduce NO emission in nitric acid production, conventional de-NO_X systems for selective catalytic reduction (SCR) NO by ammonia (UKL-7 and AK-72M plants) or non-selective by CH_4 (AK-72 plant) are used in Russia. Concentration of N_2O in tail gases depends not only on the primary platinum gauzes catalyst selectivity but on the de-NO_X conditions as well, because N_2O concentration may substantially increase in the case of SCR by ammonia. Emission of N_2O from one UKL-7 plant was found to be more than 450 tons per year. High impact of N_2O on the environment as greenhouse gas, and the international agreements and regulations require the development of efficient and economical systems for N_2O abatement in nitric acid production.

Combination of de-NO_X SCR unit with N_2O decomposition unit in one reactor is one of attractive ways. To this purpose, EnviNOx® technology developed by Uhde is the exemplary embodiment of combined removal of N_2O and NO_X from tail gas at temperatures 330-600 °C [1]. A similar combined system was proposed [2] for Russian UKL-7 plant which was comprised of vanadia-alumina de-NO_X catalyst working at 220-300 °C as the primary bed, and Fe-zeolite de-N_2O catalyst working at 350-400 °C as the secondary bed.

This work is devoted to the development of de-N_2O catalyst working at lower temperature 250-300 °C, and modeling one-reactor scheme for combined processing of NO_X and N_2O in tail gases. Experimental data on the catalytic activity of different oxide systems for N_2O decomposition at moderate temperatures are shown in Table 1. The oxide catalyst based on $Ni_xCo_{3-x}O_4$ doped with Cs cations has the spinel-like structure and is the most active and promising system for N_2O decomposition at 250-300 °C.

For combined NO_X+N_2O abatement, it was proposed to use the commercial SCR V-Al catalyst AVK-10 at the 1st stage and the proprietary catalyst under this study at the 2nd stage. Modeling of N_2O decomposition process in the 2nd bed was carried out under the following conditions that are typical for the 1st bed outlet: [N_2O] 1500 ppm, [O_2] 2.5 %, [H_2O] ≈ 3 %, [NO_X] 50 ppm, [NH_3]/[NO_X] ≈ 1.1; temperature 250 °C, pressure 0.101 MPa, GHSV 7200 h^{-1}.

Table 1. Catalytic activity of oxide catalysts for N_2O decomposition

Catalyst	T*, °C	Reaction conditions (feed gas composition, gas carrier, and GHSV)	Refs.
Fe/ZSM-5	450	700 ppm N_2O, 1000 ppm NO, 1100 ppm NH_3, 4.5 % vol. O_2, 2 % vol. H_2O, in He; 7200 h^{-1}	[2]
$Pb_{0.04}CoO_x$	414	2000 ppm N_2O, 500 ppm NO, 5 % vol. O_2, in He; 20000 h^{-1}	[3]
K - $Co_{2.6}Zn_{0.4}O_4$	350	900-1050 ppm N_2O, 400-530 ppm NO, 1100 ppm NH_3, 1-1.3 % vol. O_2, 0.3-0.5 % vol. H_2O, in He; 20000 h^{-1}	[4]
Cs - $Ni_xCo_{3-x}O_4$	300	1500 ppm N_2O, 1000 ppm NO, 1100 ppm NH_3, 2.5 % vol. O_2, 3 % vol. H_2O, in He; 7200 h^{-1}	This work

* The lowest reaction temperature at which conversion of N_2O is greater than 90 %.

The loading of the commercial reactor 3.8m ID by the catalyst in the form of 3-5 mm granules was predicted by simulation. At the bed height 0.4-0.5 m, temperature 250 °C the conversion of N_2O was no less than 98 %, thus reducing N_2O emission in tail gas to 30 ppm at the lowest.

According to the current results, a one-reactor approach for low-temperature combined abatement of nitrogen oxides at the UKL-7 plant can be realized on the existing SCR reactor in 2 consecutive adiabatic beds. Using the industrial vanadia catalyst for SCR of NO_X by ammonia in the 1st bed and Ni-Co catalyst for N_2O decomposition in the 2nd bed shall secure the expected conversion, respectively, NO_X >97 %, N_2O >98 %, thus meeting the mandatory emission levels.

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SIMULATION OF THE CATALYTIC HYDROCARBONS DEHYDROGENATION REACTOR UNDER REDUCED H_2 PRESSURE

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One way to improve the efficiency of higher paraffins dehydrogenation process for monoolefins production suitable for the production of linear alkylbenzenes is to reduce the pressure in the catalytic reactor to shift the equilibrium of the desired reaction toward the formation of the desired products. However, the pressure in the reactor is maintained by the pressure of H_2 recycle gas. Therefore, it was necessary to establish the effect of reducing the H_2 pressure on the performance of the dehydrogenation process, namely, the yield of desired products and by-products, the coke concentration on the catalyst in depends on the feedstock composition changing.

Earlier, the mathematical model of higher paraffins dehydrogenation process taking into account the instability of the process was developed [1], at the Department of Chemical Technology of Fuel and Cybernetics.

The aim of this work is to optimize the water flow for compensating the rate of dehydrogenation catalyst deactivation by coke under reduced H_2 pressure (molar ratio of H_2/feedstock).

Computer simulation was used in this research as one of the effective ways in terms of the savings in time and material costs.

Two different feedstock compositions, characterized by containing hydrocarbons C_{10}-C_{14} (feedstock 1: C_{10} – 13 % wt, C_{13} – 23 % wt, Alkylaromatics – 1.6 % wt; feedstock 2: C_{10} – 17 % wt, C_{13} – 19 wt %, Alkylaromatics – 1,2 wt %) were taken as the initial data for calculations. The calculations were performed at different H_2/feedstock molar ratio with the determination of olefins, diolefins in the reactor product stream and coke on the catalyst during the dehydrogenation changing the operating H_2 pressure in the reactor. Simulation of the reactor was carried out under the conditions that the Pt-catalyst was operated for a short time (about 80 days) in the average commodity cycle around 380-400 days, the amount of recycled feedstock amounted to about 140 000 m^3.

Table 1 – Composition of the reactor product stream depending on the H_2 pressure and the H_2/feedstock molar ratio

Feed-stock	H_2/feedstock molar ratio	Component of the feedstock, wt %	Pressure, MPa						
			0,200	0,195	0,190	0,185	0,180	0,175	0,170
1	7:1	Olefins	8,41	8,59	8,80	9,02	9,27	9,54	9,86
		Diolefins	0,53	0,53	0,54	0,55	0,55	0,56	0,57
		Coke	0,593	0,595	0,597	0,600	0,605	0,612	0,621
	6:1	Olefins	8,88	9,07	9,27	9,50	9,76	10,04	10,36
		Diolefins	0,57	0,58	0,58	0,59	0,60	0,61	0,61
		Coke	0,780	0,781	0,781	0,783	0,787	0,793	0,802
2	7:1	Olefins	8,14	8,31	8,51	8,72	8,96	9,23	9,53
		Diolefins	0,50	0,50	0,51	0,52	0,52	0,53	0,54
		Coke	0,618	0,620	0,624	0,628	0,634	0,643	0,654
	6:1	Olefins	8,59	8,77	8,97	9,19	9,44	9,71	10,02
		Diolefins	0,54	0,54	0,55	0,56	0,56	0,57	0,58
		Coke	0,811	0,812	0,815	0,818	0,823	0,831	0,842

Analyzing the data obtained, we can conclude that with decreasing H_2 pressure the content of the desired products – olefins – increases and the content of by-products – diolefins and coke on the catalyst increases. During the processing of feedstock containing more reactive – C_{13} hydrocarbons can produce more as the desired and by hydrocarbons at the same technological conditions.

Water feed to the dehydrogenation reactor helps to maintain the stability of Pt-catalyst at a relatively constant level, slowing the rate of coke formation. The consumption of water is adjusted in a certain way, and the upper limit is restricted at different temperatures of the process. To determine the optimum water flow, forecast of the catalyst commodity cycle was been made by means of the developed model. For qualitative comparison the modes of water flow in the dehydrogenation reactor at the operating (0.19 MPa) and reduced (0.17 MPa) pressure at different H_2/feedstock molar ratio were been compiled.

Table 2 – The modes of water flow when in the dehydrogenation reactor at different pressure

Temperature, °C	Pressure, 0,19 MPa				Pressure, 0,17 MPa			
	Water flow, l/hour		Coke, wt %		Water flow, l/hour		Coke, wt %	
	7/1	6/1	7/1	6/1	7/1	6/1	7/1	6/1
467,9	0	0,6	0,01	0,09	2,54	5,47	0,38	0,6
468,7	0,1	1,5	0,05	0,23	3,60	6,50	0,54	0,7
469,7	0,2	2,5	0,06	0,37	4,52	7,13	0,5	0,8
470,9	0,6	3,7	0,08	0,55	5,77	8,33	0,6	0,9
471,4	1,0	4,2	0,15	0,50	6,30	9,08	0,7	0,9
472,8	2,6	5,4	0,39	0,60	7,30	9,70	0,8	1,0
473,7	3,3	6,2	0,51	0,70	8,40	10,57	0,9	1,1
474,6	4,4	7,1	0,50	0,80	9,08	11,52	1,0	1,1
475,5	5,2	7,7	0,60	0,90	9,81	12,29	1,1	1,2
476,7	6,2	8,7	0,70	1,00	10,39	12,87	1,1	1,3
477,7	7,1	9,6	0,80	1,10	11,91	13,98	1,3	1,5
479,4	8,9	10,8	0,90	1,20	12,90	14,93	1,4	1,6
481,5	10,2	12,3	1,10	1,30	14,03	15,12	1,5	1,7

483,5	11,8	13,6	1,20	1,50	15,99	16,87	1,6	1,7
486,3	13,7	15,9	1,40	1,70	16,50	18,03	1,7	1,8

The results of the forecast turned out to be very close to the experimental results. Comparing the results obtained, it can be seen that at a reduced pressure (0.17 MPa), the water flow rate is greater than the operating pressure. A similar relationship is observed at lower H_2/feedstock molar ratio.

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KINETIC MODELING OF THE DEHYDRATION OF ETHANOL: PERSPECTIVE ON THE PATHWAY FOR THE FORMATION OF DIETHYL ETHER

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The present work addresses the dehydration of ethanol over zeolite catalyst, where main products are ethylene and diethyl ether (DEE) while some of hydrocarbons of C3+ are produced by oligomerization, cracking and hydrogenation of ethylene [1,2]. In the suggestion of kinetic mechanism for the dehydration of ethanol, two different pathways are considered; either ethanol is directly converted to ethylene or diethyl ether (DEE) is formed and then, cracked to ethanol and ethylene (cf. figure 1). For quantitative analysis, reaction rates are developed on the basis of Langmuir-Hinshelwood equation and kinetic parameters are estimated by fitting experimental data under a variety of conditions. Temperature shows positive effects on the conversion, while too high temperature decreases the selectivity of ethylene. The effects of water are also shown that the conversion is decreased with increasing water amount due to the competitive adsorption. In the feed, DEE is also included with varying amount to evaluate the role of each pathway in such a way that the developed model is used to determine the condition for maximizing the yield of ethylene.

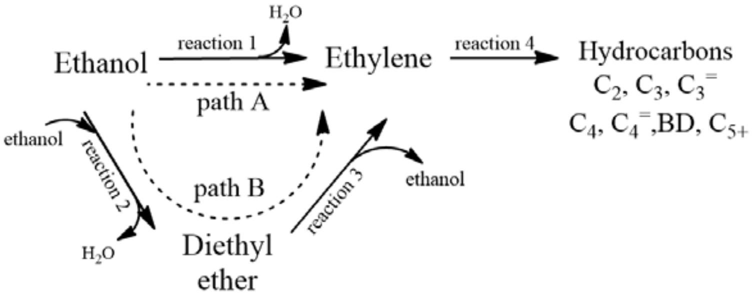

Figure 1. Kinetic mechanism proposed in the present study

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Acknowledgements

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PP-36

DESIGN OF THERMALLY COUPLED MONOLITHIC MEMBRANE REFORMER AS PORTABLE HYDROGEN PRODUCTION SYSTEM

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A thermally coupled monolithic membrane reformer (TMMR) is an integration of a reformer, a palladium membrane separator and a heat exchanger into a monolith. It was proposed as a compact unit for H_2 production. Owing to its small size and light weight, it is sutiable for portable/moblie applications. The simulations of the TMMR were examined using Gibbs reactor via Aspen Plus. Due to the absence of membrane-integrated reactor models in Aspen Plus, a sequential modular approach [1] was required. The TMMR (Figure 1) was divided into *m* sections. At *m* = 40, the results were close to the experimental data [2].

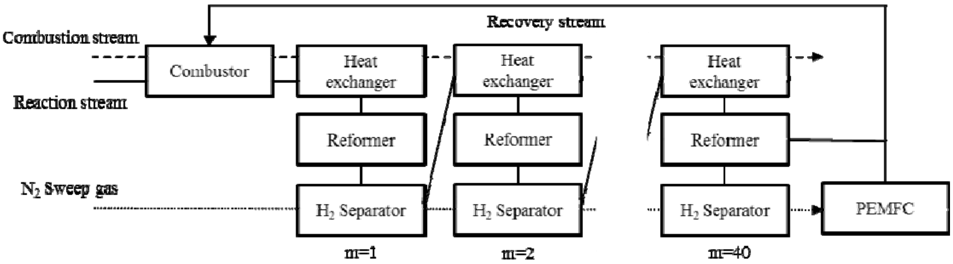

Figure 1. Sequential modular diagram

The monolith considered in this study had a cell density of 300 cpsi with a diameter of 10 cm and a length of 20 cm (1.57 L volume), and surface area of 4.78 m^2. The feeds were arranged in the checked arrangement pattern as suggested by our previous work [3]. A quarter of the total area was utilized as the heat exchanger and the separator each. The performance of the TMMR was compared with the conventional monolithic reactor using external membrane separation. Figure 2 indicates that the TMMR could improve the energy efficiency about 4.37 % on average. The use of palladium membrane helps shift forward the equilibrium reaction and therefore the near complete methane conversion of the TMMR could be achieved at lower temperature range.

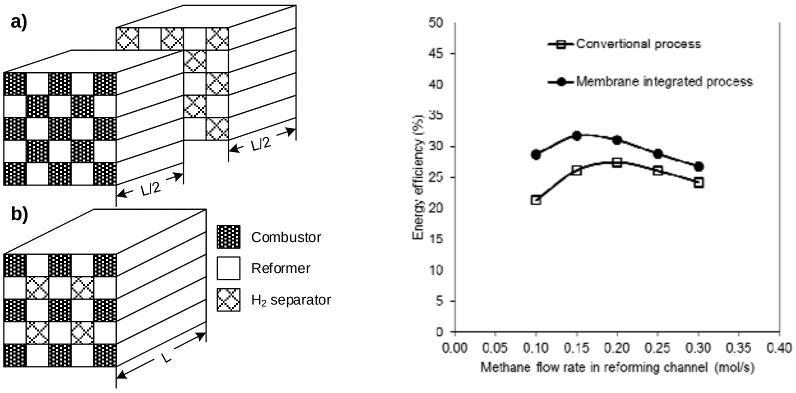

Figure 2. Comparison between conventional monolithic reactor (a) and TMMR (b)

The effect of operating conditions, i.e. fuel (CH_4) and sweep gas (N_2) flow rates and reforming pressure (Table 1) on the performance of TMMR, was further studied.

Table 1. Operating conditions

Parameters	Combustor	Reformer	Separator
CH_4 (mol/s)	0.01-0.05	0.10-0.50	-
H_2O (mol/s)[a]	-	0.20-1.00	-
Air (mol/s)	3.00	-	
N_2 (mol/s)	=	-	0.20-0.20
Pressure (atm)	1.00	1.00-5.00	1.00

[a] *S/C* = 2

High efficiency is obtained at the reforming temperature in the range of 823-973 K. In addition, H_2 permeation increased as the flow rate of the sweep gas and the reforming pressure increase, resulting in an improvement in the efficiency. At the highest efficiency, the TMMR provided 89.3 kW of H_2 and reached the efficiency of 43.6 %. Thus, TMMR is a promising unit for H_2 production in vehicles.

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PP-37

REACTION MECHANISM MODELING OF INDUSTRIAL ETHYLBENZENE PRODUCTION IN THE PRESENCE OF ALUMINUM CHLORIDE USING QUANTUM CHEMISTRY METHODS

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Ethylbenzene production is one of the leading petrochemical synthesis processes [1]. Over 70 % of produced in Russia ethylbenzene is obtained by combining of benzene with ethylene alkylation and transalkylation of benzene with diethylbenzene using aluminum chloride as a catalyst.

The purpose of this work is to study the mechanism of main and side reactions of industrial ethylbenzene production in the presence of aluminum chloride, and to determine kinetic parameters for mathematical model development of reactor.

The basic steps of quantum chemistry methods using on the example of the main process reaction are listed below. Industrial benzene with ethylene alkylation proceeds in the bubble column reactor at 393 K and 1 atm.

It is known alkylation is performed by olefin activation through the catalyst, after which the activated complex is reacted with benzene and alkylbenzenes [2]. The mechanism includes four stages. The first is reaction of ethylene with hydrogen chloride, resulting in ethyl chloride formation, which easily decays to ions: $C_2H_4 + HCl \rightarrow CH_2CH_3Cl$. The second stage is the formation of carbocation: $C_2H_5Cl + AlCl_3 \rightarrow CH_2CH_3ClAlCl_3$. At the third stage, an electrophile attacks benzene. As the result intermediate is formed which has a high energy value. It is a rate-determining stage: $CH_2CH_3ClAlCl_3 + C_6H_6 \rightarrow C_8H_{11}AlCl_4$. The last stage involves hydrogen dissociation from the intermediate, reduction of the catalyst and the product formation: $C_8H_{11}AlCl_4 \rightarrow C_6H_5CH_2CH_3 + HCl + AlCl_3$

Numerical studies were conducted using Semi-empirical method, based on NDDO (Neglecting of Diatomic Overlap) approximation at PM3 level [3] using *Gaussian 98*.

The reaction proceeds in liquid phase, therefore, the solvation effect was considered. For this Thomas model (polarized continuum model C-PCM) of limiting polarization was used. Wherethrough initial ratio of benzene: ethylene is (8-14): 1 benzene was chosen as a solvent.

The next stage is performed in products and reagents optimisation results at each step of each reaction and determination of frequencies vibration, enthalpy, entropy and Gibbs energy (Table 1).

Table 1. Products and reagents optimisation results

Substance or ion	$\varepsilon_0 + H_{corr}$, Hartree	$\varepsilon_0 + G_{corr}$, Hartree	S, kcal/(mol·K)
$AlCl_3$	-0.212299	-0.251816	72.295
$AlCl_4^-$	-0.439307	-0.491005	94.581
C_6H_6	0.142529	0.104564	69.457
CH_2CH_3Cl	0.035097	-0.000717	65.521
$C_6H_5CH_2CH_3$	0.180012	0.131055	89.564
C_2H_4	0.080951	0.053187	50.793
HCl	-0.023811	-0.04698	42.387
$CH_2CH_5^+$	0.360041	0.328737	57.271
$CH_2CH_3AlCl_4$	-0.212299	-0.251816	72.295
$[C_6H_6C_2H_5]^+[AlCl_4]^-$	-0.439307	-0.491005	94.581

Each step of the reaction corresponds to transition state. Figure 1 shows the energy profile of reaction which confirms that the rate limiting step is the formation of the third stage of transition state.

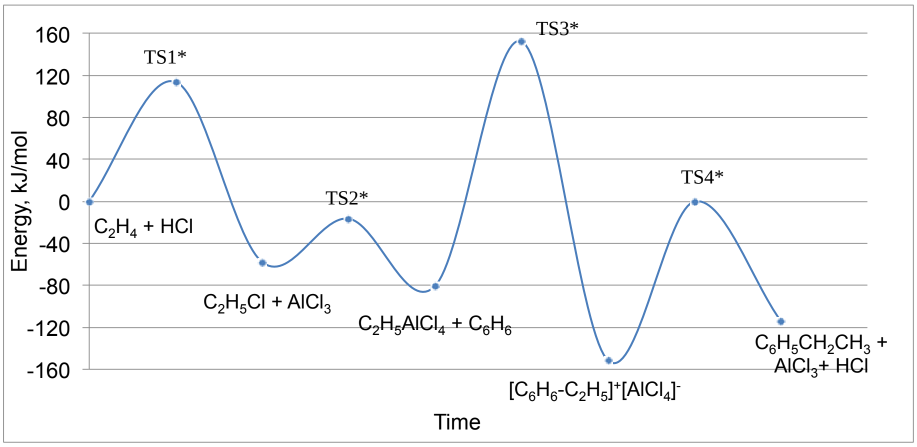

Fig. 1. Reaction energy profile

Calculations of remaining alkylation reactions were conducted in a similar way.

Obtained enthalpy, entropy, Gibbs energy and activation energy values on the basis of quantum-chemical modeling allowed to determine the kinetic parameters of each stage of benzene with ethylene alkylation. Thermodynamic and kinetic patterns are used in mathematical model development that is suitable for predicting the quality parameters of produced alkylate depending on technological mode of the process.

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PP-38

ZEOLITE BASED ETHYLBENZENE PRODUCTION MODELING

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Ethylbenzene (EB) is one of basic chemical compounds. It is used for production of styrene, ABS and SAN plastics and synthetic rubbers. In 2014 the world EB capacity was 37 Mt/y and consumption was 29.3 Mt/y [1].

The first EB production used homogeneous $AlCl_3$ catalyst. High corrosion activity, toxicity, difficulties in separation and common lacks of homogeneous catalyst were the reasons for the heterogeneous catalyst developing. Nowadays, zeolite based processes take the first place due to the techno-economic benefits in comparison to homogeneous catalyst processes.

Considerable quantity of byproducts accompanies the reaction of benzene alkylation, which is based on zeolite catalyst. Polyalkylbenzenes (dialkylbenzene (DAB), trialkylbenzene (TAB) and heavier), buthylbenzene (BB), diphenylethanes (DPE) are the main byproducts. A plant is equipped with transalkylation (TA) reactor to convert byproducts to EB. The system of both A and TA reactors is the object for optimization task because it the most effects on yield and energy consumption for purification in technology based on heterogeneous catalyst [2]. It is necessary to create a model of the system to solve optimization tasks. An industrial process data can be used if it is difficult to perform some experiments.

The method that combines chemical kinetics statements and methods of quantum-chemical calculations (QCC) for development of EB reactors math model and determination of its parameters was used. Such model allows to simulate the reactors adequately and to evaluate the decreasing of catalyst activity. It is difficult to determinate this using laboratory experiments performance. On the contrary, working parameters of an industrial scale plant like in a laboratory experiment can not be changed, which is ordinary important for parameters estimation procedure. In this case, the amount of the parameters in our model has to be maximally decreased; meanwhile it has to simulate the flow composition and process condition changes appropriately. In this work, industrial plant data for 2.5 years were analyzed. The key components that interact in chemical reactions were combined into groups that have similar nature and reactivity. For instance, o, m, p- diethyl benzenes (DEB) were combined in DEB group [3]. The groups were connected according to the final product and consumption. Thermodynamic reactions possibility (ΔG) was evaluated with QCC in *Gaussian 98*. The final reaction path way is presented in Figure 1.

Obtained kinetic equations have two or more parameters (an energy of activation, a frequency factor, an equilibrium constant) and as result, the model has some solution with some parameters combination. It is important to have precise first approach, which is close to real value. For the main reactions the parameters were defined [4]. They can be used for the first approach. However, for some reactions, such as BB, DPE formations, there is no data, but it is necessary to include these reactions in the model to predict product composition. Entropy and enthalpy for the substances formation at the process condition were defined and then equilibrium constant and reactions enthalpies were obtained. The Bronsted-Evans-Polanyi equation was used to make the first approach of the activation energy.

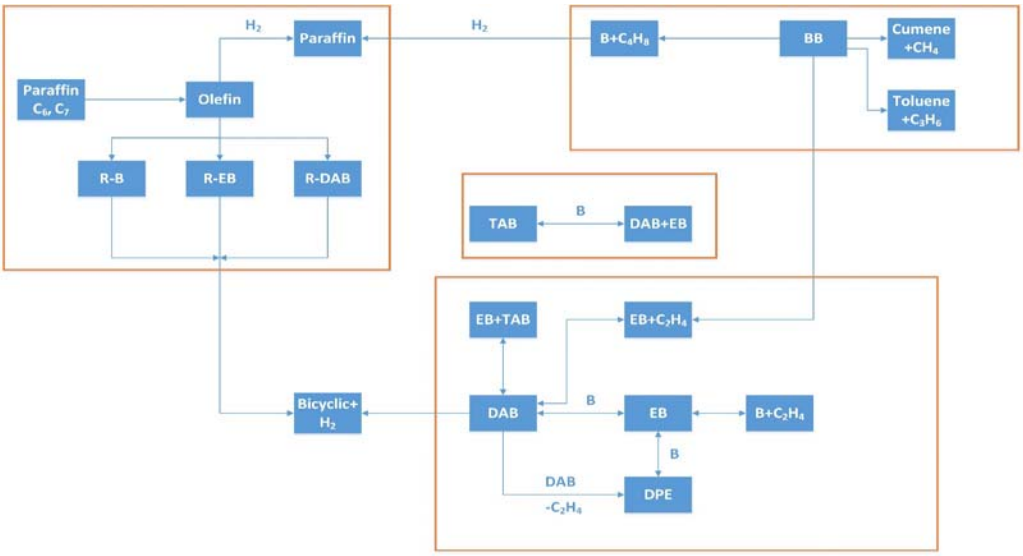

Fig. 1. The reactions pathway for TA process

The method allowed to restrict intervals for the parameters estimation in case of TA process. The combinations of parameter values were also decreased.

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PP-39

NO, CO AND C_3H_6 CATALYTIC OXIDATION ACTIVITY DEPENDING ON Pt SITES OXIDATION STATE

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Diesel oxidation catalysts containing platinum group metals (PGM) are essential components in the exhaust gas after treatment technology. They remove CO and unburned hydrocarbons (HC) and increase NO_2 concentration, which is beneficial for an effective NO_x reduction on a subsequent SCR catalyst as well as for soot oxidation by NO_2 on a particulate filter. Diesel engines are operated with lean fuel mixture (under excess of air) leading to oxidative nature of the exhaust gas. Under such conditions, the catalytic activity of platinum centres becomes affected by the formation of Pt oxides (PtO_x).

It has been reported that the catalytic NO oxidation is a reaction sensitive to Pt oxidation state – higher PtO_x coverage negatively influences the NO oxidation activity [1], Figure 1. Moreover, a negative effect of the pre-oxidized catalytic surface with higher PtO_x coverage was observed also during carbon monoxide and propene oxidation, Figure 2.

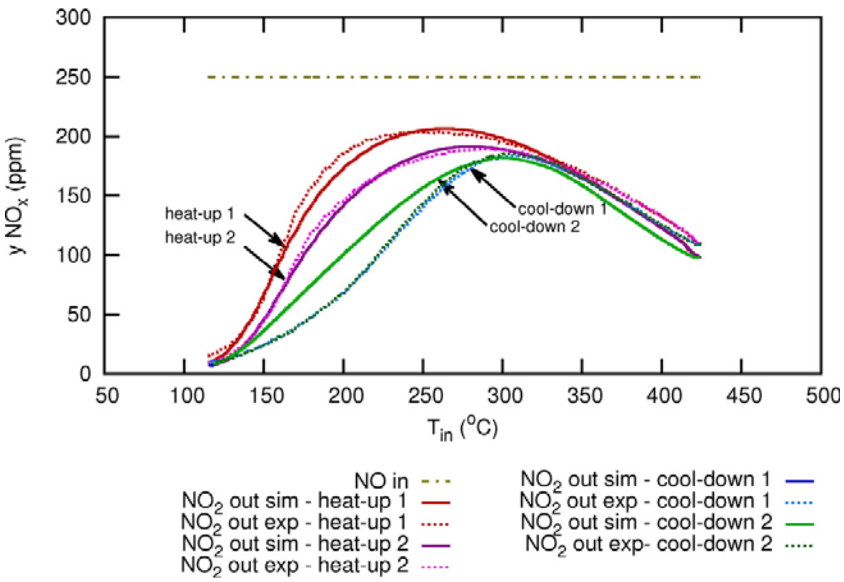

Figure 1. Experimentally observed and simulated inverse hysteresis behaviour during NO oxidation (lean feed: 250 ppm NO, 8 % O_2, 8 % CO_2 and 8 % H_2O). The run 1 is after a reductive pretreatment, and the run 2 follows immediately after the run 1. Each run consists of heat-up and cool-down temperature ramp

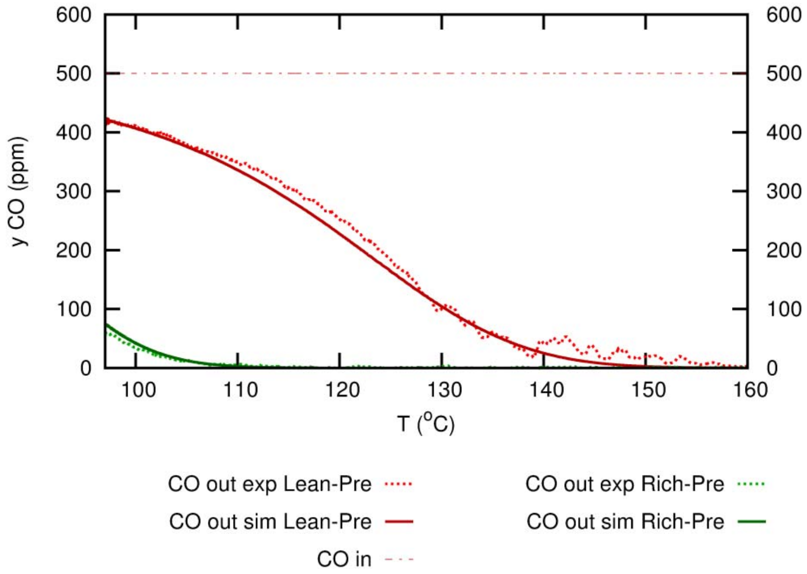

Figure 2. CO oxidation light-off depending on the initial state of the catalyst – reduced (rich pre-treatment) or oxidized (lean pre-treatment).

In this contribution we present a study exploring the impact of Pt sites state on the NO, CO and HC oxidation activity. We propose to include the dependence of catalytic activity on the Pt sites state (reduced metal vs. metal oxide) in the reaction kinetics and to extend the existing standard model for CO, hydrocarbons and NO oxidation on diesel oxidation catalyst.

The kinetics includes not only Pt oxides formation in reactions with NO_2 and O_2 but also possible mechanisms for the reduction of oxidized Pt sites: (i) spontaneous PtO_x decomposition at high temperatures, (ii) reduction by NO at low temperatures, and (iii) reduction by CO and HC pulses around the light-off temperature [1].

The extended model enables to capture the effect of the catalyst state and to predict NO, CO and C_3H_6 conversion depending on the pre-treatment or history of the catalyst operation.

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PP-40

THERMAL EXPLOSION IN SEMI-BATCH REACTORS

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The problem of thermal explosion in a semi-batch reactor is solved. According to the accepted model a cylindrical reactor is filled with a solution of reactant *A*. At the initial time, the reactor begins to be filled with the solution of reactant *B* at a constant (volumetric) rate. After the stoichiometry between *A* and *B* is reached, the feed of reactant *B* is terminated. In the reactor, a simple bimolecular exothermal reaction between *A* and *B* takes place. Heat exchange between the reactor and the environment (heat exchanger) occurs over the bottom surface and the lateral surface of the reactor, which changes during the feeding of the solution of reactant *B*. The volume of the reaction mixture in the reactor also changes during this time, resulting in a change in the concentrations of reactants *A* and *B*. Thus, the process in question is carried out in two macroscopic stages. The first stage of the reaction proceeds under conditions of feeding of reactant *B*, and the second stage under conditions of the stoichiometric ratio of reactants *A* and *B*. Thus, the process in question is carried out in two stages. The first stage of the reaction proceeds under conditions of feeding of reagent *B*, and the second stage under conditions of the stoichiometric ratio of reactants *A* and *B*.

For this model the critical conditions for the thermal explosion are studied. It is shown that the ignition resulting from the chemical reaction is possible both during the stage of feeding of the second reactant solution and after its completion. The dynamic behavior of the reactor depending on the temperature of the heat exchanger and volumetric feed rate of the second reactant is analyzed. It is shown that ignition at the feeding stage occurs at high temperature of the heat exchanger and involves two macroscopic stages. In the first stage, the temperature increases with increasing rate (thermal explosion regime), and in the second stage, its further increase occurs in the regime of combustion of second reactant. The critical ignition conditions are found to be independent on the feed rate of the second reactant in a particular range of its values.

The similar problem is solved for a semi-batch reactor in which consecutive reaction with two exothermal stages proceeds: $A + B \rightarrow C \rightarrow$ products. In this case the critical condition of thermal explosion dividing low- and high-temperature modes of a reaction, is realized only after completion of a stage of feeding of the second reactant into reactor. With increase in time of this stage the interval of transition from low-temperature mode to the high-temperature one extends with increase in Semenov criterion. Finally, the transition into regime of degenerated thermal explosion occurs.

PP-41

MODELLING OF KINETICS OF SULPHUR-CONTAINING COMPOUNDS TRANSFORMATIONS IN THE PROCESS OF HYDROTREATING

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Hydrotreating of petroleum distillates is one of the most common processes, especially removing sulfur compounds from petroleum fractions. In the catalytic hydrotreatment occurs hydrogenolysis of carbon - hetero atom with almost complete conversion sulphur-, nitrogen- and oxygen-containing organic compounds into saturated hydrocarbons with simultaneous formation of easily removable H_2S, NH_3 and water vapor.

The hydrotreating process of diesel fuel with 1.4 mass % of sulfur content is carried out with use of the laboratory catalytic setup. The aluminum-cobalt-molybdenum catalyst GKD-202 for petroleum hydrotreating is applied. The gas-liquid chromatography method is used to identify the group of sulfur compounds. The chromatograph "Kristall 2000M" was used.

On the base of experimental data the list of probable reactions was developed. The Change in Gibbs free energy considered reactions was calculated with use of software HyperChem and Gaussian. The research on determination of kinetic parameters of hydrodesulphurization was performed with using matematial modelling [1]. The general aim of this research work is to find the kinetic parameters of the chemical reactions in the process of hydrodesulfurization, and it was achieved. The activation energy is calculated for each route of chemical reactions with accent on the dynamics of such sulfur-containing hydrocarbons as dibenzotiophenes, sulfides, and benzothiophenes. Above mentioned parameters for each calculated in model sulphur-containing compounds are presented in Table 1.

It should be noted a regular decrease activity of sulfur-containing compounds with increasing their molecular weight. The rate constant for the hydrogenation of individual SS connected with the change of the Gibbs energy. The obtained rate constants of benzothiophenes and dibenzothiophenes to increase with decreasing molecular weight of the molecule and, respectively, with an increase in modulus of the Gibbs energy change. On the basis of the data presented in Table 1 the hydrogenation rate of sulfur compounds decreases: sulfides > benzothiophenes > dibenzothiophenes that is also confirmed by the literature data [2,3].

Table 1. The change in Gibbs free energy and rate constants of sulphur-containing compounds

№	Change in Gibbs free energy, ∆G, kJ/mol	Rate constant, k, h^{-1}	Reaction
1	-95,3	2,114	$C_9H_9S + 3H_2 \rightarrow C_9H_{13} + H_2S$
2	-83,5	2,065	$C_{10}H_{11}S + 3H_2 \rightarrow C_{10}H_{15} + H_2S$
3	-71,1	1,956	$C_{11}H_{13}S + 3H_2 \rightarrow C_{11}H_{17} + H_2S$
4	-65,1	1,907	$C_{12}H_8S + 2H_2 \rightarrow C_{12}H_{10} + H_2S$
5	-54,3	1,877	$C_{13}H_{11}S + 2H_2 \rightarrow C_{13}H_{13} + H_2S$
6	-53,7	1,761	$C_{14}H_{13}S + 2H_2 \rightarrow C_{14}H_{15} + H_2S$
7	-49,4	0,968	$C_{15}H_{15}S + 2H_2 \rightarrow C_{15}H_{17} + H_2S$

The developed mathematical model is based on the law of mass action which represents the system of differential equations and reflexes the change in concentrations of reacting substances.

Modelling is based on experimental data obtained from monitoring of industrial LG-24/7 hydrotreating set using the obtained values of the rate constants were made. The relative error in the calculations, using data for the whole period of monitoring the installation LG-24/7 was not more than 5 % of the total content of sulfur in the product hydrotreating.

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PP-42

AEROBIC EPOXIDATION OF SUNFLOWER BIODIESEL USING TRANSITION METAL COMPLEX CATALYSTS

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Currently the methods of epoxidation of vegetable oils and their derivatives with using special agents (peracids, organic hydroperoxides, hydrogen peroxide [1,2,3]) are well-known. In this report applying an atmospheric oxygen as an epoxidizing agent was proposed. Air oxygen as a single oxidant in the reaction mixture is rather desirable as available and absolutely non-toxic oxidant. The aim of this work was to study the kinetics of the process of epoxidation of the mixture of fatty acid methyl esters of sunflower oil by atmospheric oxygen.

It has been assumed that peroxide compounds, which form in situ through the radical oxidation, can epoxidize double bonds of unsaturated fatty acid esters in the presence of transition metal complex [4]. The complexes of cobalt, molybdenum and vanadium with glycols (propylene glycol and diethylene glycol) were considered as the catalysts.

Cobalt catalyst, accelerating peroxides forming, demonstrates typical properties of oxidation catalyst. In addition, the rate of peroxides cleavage side reactions enhances with increase of temperature. The epoxide selectivity is lower than 12 %.

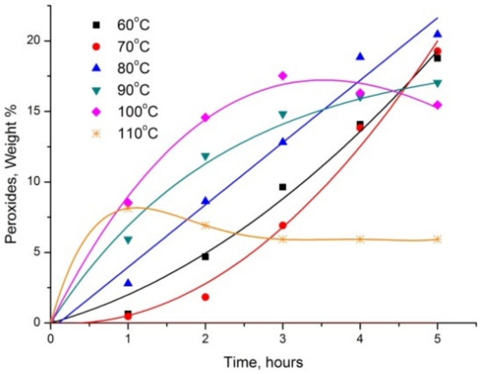

Fig. 1. Peroxides forming at the different temperatures in the presence of Co-catalyst

The epoxide selectivity increases substantially in the presence of molybdenum (VI) complex. It has found out that changing of process parameters in the reaction mixture with Mo-catalyst (temperature, air consumption, catalyst concentration) doesn't affect on the way of the process, i.e. concentration of epoxides achieves certain value, after that the rate of epoxides forming decreases, simultaneously the rate of side reactions enhances sharply. Thus, the epoxide selectivity diminishes with increase of biodiesel C-C double bonds conversion. The highest yield of epoxides was 20 %. As opposed to Co-complex, molybdenum complex doesn't accelerate the reactions of peroxide compounds forming (peroxides forming is caused only by radical mechanism). It should be noted, that different analysis (chromatography, IR, NMR-spectroscopy) haven't been detecting hydroxyl-compounds in the reaction mixture, therefore the tradition mechanism of olefin substances epoxidation catalyzed by transition metal complexes has not been confirmed.

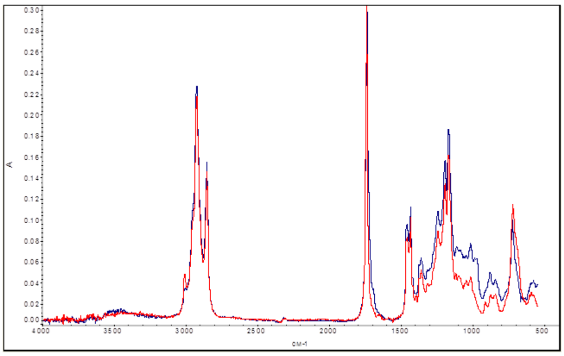

Fig. 2. IR spectra: red line – FAME; blue line – FAME epoxidized on Mo-catalyst

When the vanadium complex is used as the catalyst, the rate of peroxides generation is the lowest and declines with the increase of unsaturated compounds conversion. In this case, unlike a Mo-catalyst, the yield of epoxides is twice as low. The specific feature of V-catalyst is more intensive process of cleavage products forming compared with a Mo-catalyst. Significant quantity of hexanal has been detected in the mixture of products obtained through the reaction of a sunflower biodiesel with air oxygen in the presence of V-complex.

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The IR and NMR spectra were carried out on the equipment of The Center for Collective Use of D. Mendeleev University of Chemical Technology of Russia.

PP-43

DIRECT AMINATION OF ALCOHOLS WITH AMMONIA

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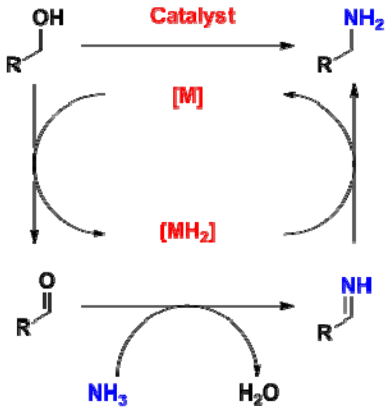
Amines constitute an important class of organic compounds and intermediates in the chemical industry. These important building blocks find applications in a wide variety of products such as polymers, solvents, surfactants, agrochemicals, and pharmaceuticals. Various approaches have been developed for the synthesis of organic amines such as reduction of nitriles, amination of alkyl halides, reduction of nitro compounds, hydrocyanation of olefins and reductive amination of carbonyl compounds [1]. The direct amination of alcohols with ammonia is the most attractive way to produce amines since water is the only by-product generated [2, 3]. The overall transformation is highly atom-efficient and economical. In this work, the continuous high-pressure amination of alcohols with ammonia over heterogeneous catalytic systems was investigated and the influence of reaction variables on the product selectivities will be elucidated. The proposed reaction mechanism which proceeds via a hydrogen borrowing mechanism (Scheme 1) is described based on the experimental data.



Scheme 1. Direct amination of alcohols through the borrowing hydrogen mechanism

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A NOVEL METHOD TO PREPARE Zn/Cr MIXED OXIDE CATALYSTS BY FLOW SYNTHESIS OF HYDROTALCITE PRECURSORS

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Performance of various mixed oxide catalysts scales with specific surface area and degree of molecular dispersion among cations. Our synthesis approach uses structure imposed cation dispersion in high surface area hydrotalcite (HT) precursors to obtain copper-free mixed oxide catalysts with outstanding performance in methanol synthesis. Numbering-up capability and continuous HT making is achieved by optimized flow synthesis avoiding common shortcomings of conventional preparation. Common techniques to prepare HT include co-precipitation synthesis [1-2], urea hydrolysis [3-4], hydrothermal treatment [5-6] and sol-gel method [7-8]. These synthesis techniques are simple and require only modest investment, but cause high-energy cost and show low scalability on other hand.

Three flow synthesis routes were assessed in ZnCrHT preparation using “decreasing pH (F1)”, “increasing pH (F2)” and “constant pH (F3)”, respectively. Synthesis temperature was controlled at 80 °C and aging time in tube coils was fixed to 10 min, 15 min and 30 min. ZnCrHTs obtained by flow synthesis configurations showed much higher surface area (Figure 1), sharper pore size distribution and more regular particle structure than co-precipitation samples made under the similar conditions. The highest surface area is achieved via “increasing pH (F2)” and the lowest by “decreasing pH (F1)” preparation. For each configuration, the surface area increased with rising aging time at the expense of precipitate yield. Catalytic performances of mixed oxide catalysts obtained from calcined ZnCrHTs were evaluated with the synthesis of methanol from syngas. The surface area of calcined ZnCrHTs obtained by flow synthesis showed the same trend as the ZnCrHTs before calcination. Results on CO conversion and methanol selectivity are shown in Figure 2. Flow synthesis made catalysts show higher CO conversion and methanol selectivity than those prepared by co-precipitation. Enhanced surface area of hydrotalcite precursors had a significant positive role in promoting the catalytic performance although the double layer structural feature was lost during calcination.

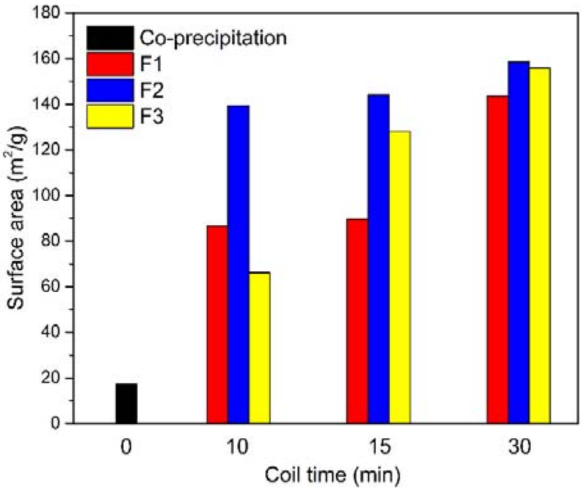

Figure 1. BET surface area of ZnCrHT obtained by co-precipitation and flow synthesis

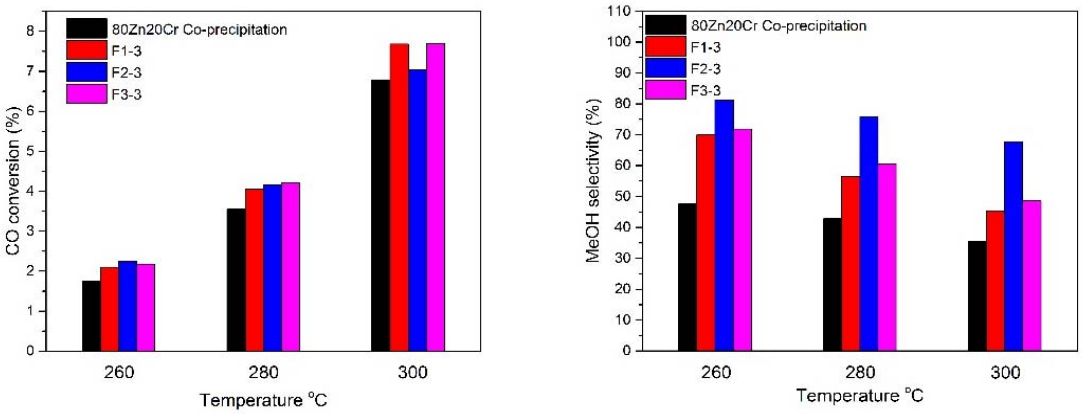

Figure 2. CO conversion and methanol selectivity at 260 °C, 280 °C and 300 °C

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THEORETICAL PREDICTION OF EFFECTIVE DIFFUSION-REACTION PARAMETERS OF A ZEOLITE CATALYST PARTICLE

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Zeolite catalysts are widely applied in industrial sectors, such as fluid catalytic cracking (FCC) and methanol to olefins (MTO). In order to model these catalytic reaction processes, some effective fundamental parameters of zeolite catalyst particles, such as diffusion-reaction coefficients, are required. The classical scheme to derive these coefficients is normally based on experimental data fitting. Its application scope is highly dependent upon the experimental conditions, and the reliability of the kinetic model is highly related with researcher's experience. The experimental conditions which are generally not so ideal will make researchers suffer numerical puzzle in fitting experimental data. In this paper, a hierarchical multi-scale approach instead of real experiment was used to fit diffusion-reaction parameters. And a more convenient numerical scheme based analytic solutions was proposed by constructing ideal virtual experiment conditions.

Recently, we proposed a modeling approach to simulate the diffusion-reaction processes in both micro-pores and macro/meso-pores simultaneously [1]. Since the catalyst pellet contains a variety of small micro-pore zeolite crystal particles (active sites) which are dispersed in macro/meso-pore catalyst support (or called matrix), the model should be able to deal with different diffusion mechanisms (including bulk, Knudsen and surface diffusions) dwelled in different pore sizes. From the view of modeling hierarchy, this model could be regarded as a meso-scale model (medium level). Here, Micro-scale models are at the lowest level for catalyst particles, their research objects focus only on zeolite crystals. Keil [2] and Hansen and Keil [3] proposed such a model for decribing diffusion-reaction process in zeolite crystals by coupling different scales of quantum chemistry, force field simulations and macroscopic differential equations. Macro-scale models are at highest level for catalyst particles. The main feature of this model is to assume uniform distribution of reaction sites and the same diffusion mechanism inside the whole catalyst particle [4]. The aim of this paper is to derive the effective diffusion-reaction parameters of macro-scale model from a series virtual experiments based on our meso-scale model. This means that the meso-scale model could act as a bridge between macro-scale model and micro-scale model.

Here, as an example, we predicted effective diffusion-reaction parameters of alkylation of benzene with ethylene over AB-97 zeolite catalyst [5]. For macro-scale model, the control equations of ethane, benzene and ethylbenzene could be written as

$$\frac{\partial}{\partial t}\begin{pmatrix}\tilde{c}_1\\ \tilde{c}_2\\ \tilde{c}_3\end{pmatrix} = \nabla \bullet \begin{pmatrix}D_{11} & D_{12} & D_{13}\\ D_{21} & D_{22} & D_{23}\\ D_{31} & D_{32} & D_{33}\end{pmatrix}\begin{pmatrix}\nabla\tilde{c}_1\\ \nabla\tilde{c}_2\\ \nabla\tilde{c}_3\end{pmatrix} + \begin{pmatrix}-1\\ -1\\ 1\end{pmatrix}\tilde{r} \tag{1}$$

$$\tilde{r} = k_f \tilde{c}_1^{\,n_1} \tilde{c}_2^{\,n_2} - k_r \tilde{c}_3^{\,n_3} \tag{2}$$

where D_{ij}, k_f, k_r and n_i are effective parameters of the zeolite catalyst pellet. In order to fit D_{11}, we could find an analytic solution

$$\begin{cases}\tilde{c}_2 = \text{constant}, \tilde{c}_3 = \text{constant}, \tilde{r} = 0\\ \tilde{c}_1(t,x) = \tilde{c}_{1,\text{ref1}} + \tilde{c}_{1,\text{ref2}} e^{-D_{11}\left(\frac{\pi}{L}\right)^2 t} \sin\frac{\pi}{L}x\end{cases} \tag{3}$$

This solution provides an ideal virtual experiment condition by fixing the concentrations of species 2 and 3 and setting $\tilde{r} = 0$. Only concentration of species 1, with initial value $\tilde{c}_{1,\text{ref1}} + \tilde{c}_{1,\text{ref2}} \sin\frac{\pi}{L}x$, evolves along with time in the simulations based on the meso-scale model. On the basis of the simulated results of species 1, D_{11} could be easily fitted according to eq. (3). It is similar to derive D_{22} and D_{33}. Other parameters are also could be easily fitted by constructing corresponding ideal conditions in the similar way.

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CFD SIMULATION OF BUBBLING FLUIDIZED BED USING A LOCAL-STRUCTURE-DEPENDENT DRAG MODEL BASED ON EMMS THEORY

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Gas-solid bubbling fluidized bed reactors are of great importance in numerous industrial applications including granulation, catalytic cracking and methanation because of their excellent heat and mass transfer performance [1]. In order to accurately simulate the hydrodynamics in bubbling fluidized bed using two-fluid model (TFM), it is necessary to take the impacts of meso-scale structure on drag force into fully consideration [2]. Fortunately, energy-minimum multi-scale (EMMS) theory was developed to describe gas-solid interaction, in which drag force is expressed as a strong function of structure parameters [3]. So far, researchers have done extensive work on the mechanism how flow structure influences the drag force [4-6]. Although the simulation results obtained by previous drag models correspond to the experimental data, these models still lack the systematisms and established based on many assumptions. Above all, there is a crucial contradiction in these models because they calculate drag force using structure parameters in whole bed section when modeling while using the local grid information when coupled with CFD solver.

Given these problems, a local-structure-dependent (LSD) drag model based on EMMS theory is established to unify the using of structure parameters and systematically investigate the gas-solid interaction. In LSD drag model, six fundamental equations including particle force balance equations in three sub-systems (emulsion phase, bubble phase and interphase), gas force balance equation (i.e. pressure-drop balance equation), slip velocities correlation and local mean voidage equation are obtained in the computational cell. There are ten unknown variables (ε_e, ε_b, a_{pe}, a_{pb}, a_b, f_b, $u_{slip,e}$, $u_{slip,b}$, $u_{slip,i}$, d_b) contained in the six fundamental equations. So, stability condition should be established to close the model according to the basic conception of EMMS theory that suspension energy consumption of gas-solid system tends to be minimum. Then, the nonlinear programming problem made up by fundamental equations and stability condition is solved by genetic algorithm (GA). Eventually, as a function of local mean voidage (ε_g) and local slip velocity (u_{slip}), the solved drag coefficient (β) is coupled with CFD solver to simulate the hydrodynamics of Geldart A~B particles in bubbling fluidized bed. The simulated results of LSD drag model shows an obvious agreement with experimental data [7-9] compared with that of conventional Gidaspow model, as shown in Figure 1. Also, LSD drag model interprets the assumptions of pervious drag model and gives an integrated investigation on gas-solid interaction.

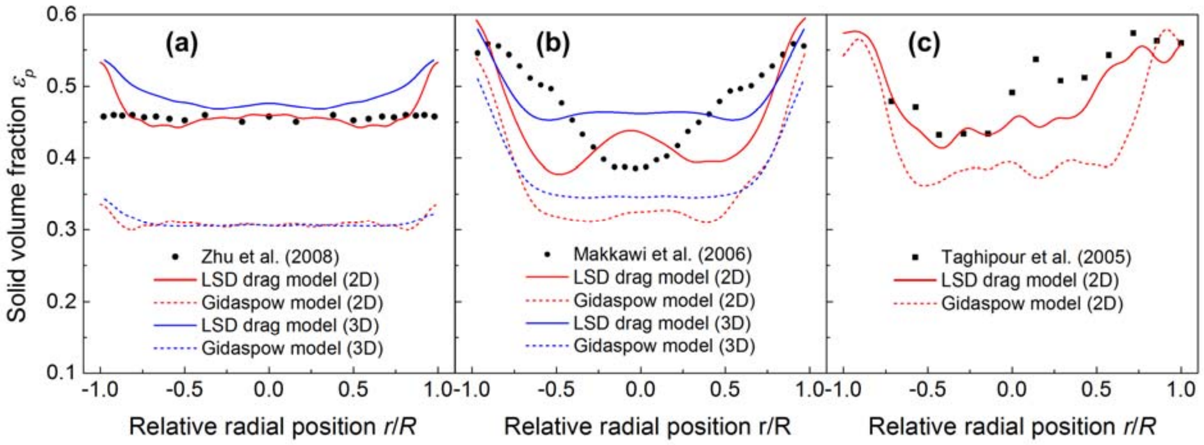

Figure 1. Comparison of simulated and experimental solid volume fractions of
(a) Geldart A (U_g = 0.06 m/s, h = 0.4 m),
(b) Geldart A/B (U_g = 0.26 m/s, h = 0.143~0.181 m) and
(c) Geldart B (U_g = 0.38 m/s, h = 0.2 m)

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PP-47

ESTERIFICATION SYNTHESIS OF BIODIESEL OVER SILICA-SUPPORTED HETEROPOLYACID PREPARED BY IMPREGNATING AND IN-SITU SOL-GEL METHODS

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Introduction

Heteropolyacids (HPAs) can be used in homegeneous and heterogeneous catalysis due to special physcoichemical properties, such as high solubility in water and organic solvents, pseudo-liquid phase behavior and catalytic activity and selectivity designed easily in molecular level. However, supported HPAs, as heterogeneous catalysts, are of greater value for practical applications than homogeneous HPAs because they are easy to recovery and reuse during reaction processes. On the other hand, the use of supports makes HPAs be dispersed over a large and special surface, which may greatly increase the catalytic activity and selectivity in some acid-catalyzed reaction related to surface area and pore structure. It was also reported that the acid strength of supported HPW decreases according to the following order: SiO_2 > Al_2O_3 > carbon, as a strong interaction may exit between HPW and activate carbon. The supported HPW on SiO_2, SiO_2-Al_2O_3 or r-Al_2O_3 remains the primary Keggin structure, but partial degradation emerges in the support containing Al_2O_3 [1]. SiO_2 is the most usual and efficient support thanks to its relatively inert, large surface area and effective resources, to prepare supported HPAs for esterification of fatty acid to biodiesel [2]. In this paper, supported HPW catalysts were prepared from a variety of artificial and natural silica resources by impregnating method and in situ sol-gel method. The catalytic performance of catalysts obtained was measured by esterification of fatty acid and methanol to biodiesel, and the interaction between SiO_2 and HPW were studied in detail.

Experimental/methodology

The mantmorillonite clay or diatomite was activated by 6.0 mol/L HCl leaching treatment at a temperature of 353 K, distilled water washing, drying in vacuum and following calcination at 673 K. Impregnating method: supported catalysts were prepared by impregnating 10 wt % HPW ethanol-water solution (50 % V/V) on silica materials with a ratio of 20 wt % HPW/SiO_2 and evaporating water at 353 K, then dried at 393 K for 4 h.

In-situ sol-gel method: a HPW catalyst included in SiO_2 matrix was obtained by mixing of colloids silica and 20 wt % HPW ethanol-water solution with a ratio of 20 wt % HPW/SiO_2 and evaporating water at 353 K, then dried at 393 K for 4 h. In addition, tetraethyl-orthosilicate was added into 10 wt % HPW ethanol-water solution, according to a ratio of 20 wt % HPW/SiO_2, and stirred at 353K for 2 h. After the mixture was evaporated at 353 K and dried at 393 K for 4 h, another HPW catalyst included in SiO_2 matrix was finished.

The esterification reaction of fatty acid and methanol to biodiesel was performed under atmosphere pressure at 343 K in a multi-necked flask with magnetic stirrer. The mixture of 1.2 g supported-catalyst powder (< 60 mesh) or 0.24 g hexadydrate HPW, 14.2 g C_{18} fatty acid and 8.0 g methanol reacted for 4 h. The products of esterification were analyzed by GC with FID and an OV-101 fused silica capillary column.

Results and discussion

The surface area of the acidified diatomite is very small, only 5.8 (61) m^2/g, but other supported HPAs are of a large surface area, increasing according to the following order: included in SiO_2 matrix from tetrarthyl-orthosilicate > supported on > supported on acidified clay > included in SiO_2 matrix from SiO_2 colloid. Except for HPW included in SiO_2 matrix prepared from tetrarthyl-orthosilicate, there are little microporous pores in other supported HPW. XRD patterns indicate that there is neither peak related to pure HPW crystal in supported HPW catalysts, nor other crystalline phases were detected except for the supported HPA on acidified diatomite. On the other hand, it is seen that there is some difference among XRD patterns of these supported-catalysts, which reflects properties of different structural silica supports. FT-IR spectra show that there are absorption bands at 1080-1 (P-O), 982-5(W=O), 898-7, 802-3 (W-O-W), 600 and 532 cm^{-1} for all supported HPW, which are characteristic of the HPW heteropolyanion vibrations. Therefore, Keggin structure of HPW supported on surface of SiO_2 or included in SiO_2 matrix is retained. However, besides above typical bands of HPW, a weak band at 1232 cm^{-1} indicates the partial decomposition of HPW supported on acidified clay. For HPW included in SiO_2 matrix, a blue shifted ca. 25 cm^{-1} of the bands for outer groups (W=O, corner- and edg-bridging W-O-W) is observed with respect to the crystalline heteropolyacid at 799 cm^{-1}. 31 P MAS-NMR spectra show that there is more or less line broadening and small chemical shift moving compared with pure HPW, which clearly indicates that the light interaction with varying degree exists between HPW and SiO_2. With respect to HPW included in SiO_2 matrix from tetraethyl-ortsilicate and silica colloid, their line boradening is hardly observed, which reflects that HPW is dispersed very uniformly, possibly in molecular unit.

The results of esterification reaction show that there are great differences among catalytic performance of supported HPW though HPW was loaded on silica source at the same content. The bulk HPW and supported HPW on Grace porous SiO_2, are of the highest catalytic activity, whereas supported HPW on acidified clay is the lowest catalytic activity. After catalysts were reused for two times, the catalytic activity of supported HPW on surface of SiO_2 was decreased, especially for the supported on acidified diatomite. However, the catalytic activity of HPW included in SiO_2 matrix remains stable, without an appreciable decrease. On the other hand, HPW included in SiO_2 matrix from tetraethyl-orthosilicate is of the highest selectivity of biodiesel. Interestingly, HPW included in SiO_2 matrix from tetrarthyl-orthosilicate is not only of a large surface area, but also of a micropore structure with narrow pore distribution. It may be considered that 20 wt % HPW of HPAs included in SiO_2 matrix was highly dispersed in silica matrix. HPW polyanion may play a template role similar to surfactants in synthesis of mesoporous material. On the other hand, when tetrarthyl-orthosilicate is replaced SiO_2 colloids as SiO_2 resource, a macropore catalytic material with a narrow pore distribution is obtained. Therefore, it may be inferred that the structure formed is related to the interaction between HPW and SiO_2 sol-gel in solution.

Conclusion

All supported HPW with 20 wt % HPW/SiO_2 obtained highly dispersed HPW catalysts, except for acidified diatomite with low surface area, and their structure formed is related to the interaction between HPW and SiO_2 sol-gel. The supported HPW on Grace porous SiO_2 show the highest catalytic activity, whereas supported HPW on acidified clay is the lowest catalytic activity. HPW included in SiO_2 matrix has the highest selectivity of biodiesel.

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PP-48

OXIDATIVE REFORMING OF BIOFUEL TO SYNGAS IN THE SELF-SUPPORTED $Ba_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_{3-\delta}$ MEMBRANE REACTOR

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$A_{1-x}Sr_xCo_{1-y}Fe_yO_{3-r}$ (A = La or Ba) perovskite-type oxides have been used as electrodes for solid oxide fuel cells and ceramic membrane for oxygen separation. Application in high temperature electrolysis and catalytic partial oxidation reactors make use the unique characteristics including high oxygen selectivity, ionic conductivity and long term stability [1]. Conventionally the perovskite substrate is prepared by solid-state reaction (combustion) [2], sol-gel [3], polymetric gelation [4] and co-precipitation (in batch) [5]. Unfortunately, the latter routes are limited in terms of energy consumption and scaling to industrial dimension. In turn, there is only little use in chemical industry despite self-supported membrane reactor technology being a highly promising concept.

This study describes continuous flow synthesis in micro-channels yielding alkali–free $Ba_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_{3-\delta}$ perovskite-type oxides. The route is compared a conventional batch process yielding cost effective synthesis only at the expense of lower material quality. We demonstrate synthesis of pure perovskite in form of crystalline particles (0.1-0.8 μm) with less Sr loss favourably comparing to larger particles (0.2-1.1 μm) with more impurities generated by the batch process. Superior efficiency of flow synthesis can be attributed to precipitation with homogeneous metal distribution resulting from rapid mixing and enhanced mass transfer in a microchannel. Fabrication of disk-shaped self-supported membranes from the perovskite-type oxide is demonstrated. Membranes are made of the achieved perovskite and are assembled to membrane reactor examined in oxidative steam reforming of biofuel to syngas.

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MULTICOMPONENT DIFFUSION WITH CHEMICAL REACTION IN A POROUS MEMBRANE: TRANSIENT MODELLING OF THE CATALYTIC DECOMPOSITION OF HCOOH COUPLED TO THE WATER-GAS SHIFT REACTION

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This is a theoretical study of the transient behaviour of two continuous stirred tank reactors (CSTR) linked by a porous catalytic membrane. In each of the CSTR a different catalytic reaction takes place, and a third different reaction occurs within the catalytic membrane. The reactions performed in each of the two CSTR are the dehydrogenation of formic acid on MgO to produce H_2 and CO_2 and the oxidation of formic acid on SiO_2 to produce H_2O and CO [1]. The reaction products from the CSTR´s are the species involved in the water-gas shift reaction (WGSR), which is assumed to take place within the catalytic membrane [2-4]. Moreover, the reactions taking place in each CSTR and at the membrane occur at different temperatures.

Our aim is to compare different reaction kinetic schemes for the WGSR in the catalytic membrane, which in turn is coupled to multicomponent diffusion, modelled by the dusty-gas model [5]. In this way, once the diffusion in absence of the WGSR has been characterised, different kinetic models (from the literature), can be compared. The structured reactor set-up operates initially with a feed of the same amount of formic acid and N_2 at each reactor, and after some TOS the operation changes by suppressing the feed of formic acid and N_2, and the new feed is now composed of similar amounts of H_2O, CO, H_2 and CO_2 that feed indistinctly at each of the CSTR´s, to follow up the dynamics of the reaction within the catalytic membrane, which is 1cm thick. In this way, reactants and products of the WGSR meet, coming from either sides of the membrane and react. The reactions in the CSTR´s are assumed to take place on externally deposited catalysts where intra-particle diffusion is not limiting. The reaction at selected points in the catalytic membrane is then calculated as well as the concentration profiles of the six-gas component mixture. The transient model is solved by orthogonal collocation for the membrane, and the numerical integration evaluates the average rate of reactions for each of the WGSR kinetics.

In this work, two different kinetic schemes are considered for the WGSR: one uses a Langmuir-Hinshelwood type of expression, as developed by Choi and Stenger, and by Wei-Hsin, et al. [2, 4], whereas the other considers a two-reaction step scheme of the redox type, like the one proposed by Temkim et al. [3, 4].

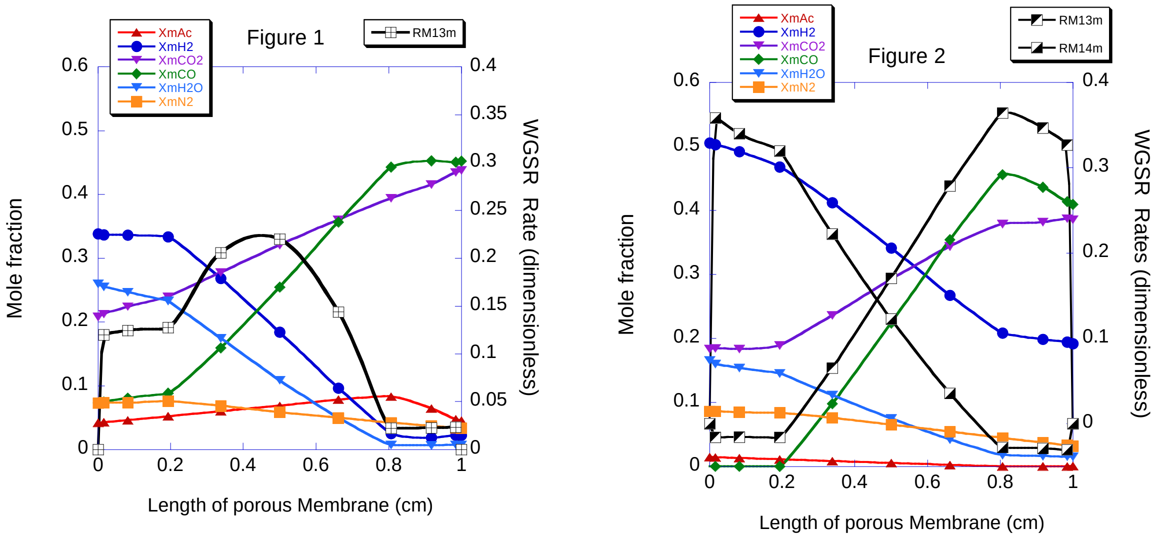
Scheme 1: $$R = k\left(C_{CO}C_{H2O} - C_{CO2}C_{H2} / K\right) \tag{1}$$

Scheme 2: $$R_1 = k_1\left(C_{CO}\theta_O - C_{CO2}\theta_R / K_1\right) \tag{2}$$

$$R_2 = k_2\left(C_{H2O}\theta_R - C_{H2}\theta_O / K_2\right) \tag{3}$$

In the above expressions R is given in (moles/cm^3 sec) whereas R_1 and R_2 are given in (moles/cm^2 sec); and θ_O and θ_R are the fractions of oxidised and reduced sites, respectively.

Figures 1 and 2 show the mole fraction profiles of the six-gas species and the magnitude of the reaction rates within the membrane after 880 sec of a transient operation at an isothermal membrane temperature of 523 K. Initially, smaller amounts of HCOOH and N_2 were fed to both CSTR´s, and H_2O and CO were fed in equal amounts to CSTR-1, whereas at the same time equal amounts of H_2 and CO_2 were fed to CSTR-2. Then, after 660 sec the fed to both CSTR´s is changed, and now H_2 and H_2O are fed in equal amounts to CSTR-1, whereas at the same time equal amounts of CO and CO_2 are fed to CSTR-2. Finally, the feed concentrations for both CSTR´s are reversed to its initial values after 1300 sec of transient operation. It can be observed that the rate given by equation (1) in figure 1 dominates the central part of the membrane and it is of smaller magnitude, whereas the rates in equations (2) and (3), of larger magnitudes, are displaced to the extremes of the membrane, according to where reactants and products meet for the reversible WGSR. As observed, the magnitude of mole fractions is also different, showing the effect of a more detailed kinetic scheme for the WGSR. The calculations of mole-fraction profiles in absence of the WGSR at same conditions (not shown), allows the comparison of the impact of the multicomponent diffusion coupled to the catalytic reaction for each of the kinetic schemes. It is important also for our studies to compare the validity of using Fick´s law of diffusion when dealing with a multicomponent mixture for these reaction systems. Model simulations at different temperatures will allow us to assess different kinetic models, and in this way different kinetic schemes can be tested. Because a membrane of 1 cm thick may be considered excessive, smaller sizes can be used, however the effect of the membrane size is important in the yield of H_2, as it was observed.



Figures 1 and 2. Comparison of the two reaction schemes, showing mole fraction profiles at the porous catalytic membrane for the WGSR at T = 523 K at 880 sec. Figure 1 refers to the WGSR in equation (1), and figure 2 to the reactions in equations (2) and (3).

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PP-50

MATHEMATICAL MODEL FOR HEAP LEACHING OF OXIDES COOPER

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The heap leach ore and has gained columnseconomic significance for the value of the final product of the extraction process is copper, but also by the use of sulfuric acid as extracting agent, which can be reused. The scientific contribution to this area is to find the solution of mathematical models to predict the behavior of these systems with the aim of improving the economic and environmental process. In this paper a number of three phases reactors correlations and numerical prediction for a good approximation of the behavior of the system were implemented. The methodology followed is summarized in pose and solve a model for mineral particles, a model and resolution for the extracting agent, the assembly of both, then the inclusion of correlations for calculation of parameters, all setting with the help of data obtained in plant laboratories. All this resolved FORTRAN® codes and making combined use of orthogonal collocation and finite differences.

It was obtained a mathematical model that includes the phenomena transport within the mineral and the leach solution, you can meet over time the concentration profile inside the particle at any level of the particle. It is also possible to predict the concentration of copper in the leaching solution at any level of the particle. Correlations have been applied for percolation reactor systems and well adjusted prediction data and ground, so that it has eliminated the need for optimization subroutines. Another contribution of this work is to have found convergence by combining the techniques of orthogonal collocation and finite differences.

They can study the influence of particle size, height of the heap and recirculation of solutions. The equations are proposed for each reacting species. Also the initial and boundary conditions. This research is planned to be developed in four stages.

1) Verification of mineral components, definition of variables and hydrodynamic processes, proposed numerical techniques: orthogonal collocation.

2) material balance for sulfuric acid and correlations selection Giannetto and Specchia (1992), and Drinkenburg Rao (1985), and Wakao and Smith (1962), Bird et al (2002), testing with orthogonal collocation solution.

3) Resolution of the interparticle model for the concentration profiles in the packaging for both phases, and also to intraparticle level.

4) Implementation of an optimization routine to adjust parameters and validate the model plant information.

We have simulated the diffusion of copper through the particle, regardless of the reaction pathways and dissolution also the effects of the free stream. The results show an average error of 20 % of the results of experimental processes in which the particle radius is greater than 3 cm and more average error results in processes in which the particle radius is less than 3 cm.

Is displayed it is possible to obtain a better approximation when the competence of the reactions of various minerals (copper and other metals) is included as part of the model that corresponds to the free stream is included.

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OXIDATIVE CONVERSION OF C3-C4 HYDROCARBONS OVER POLYCOMPONENT OXIDE CATALYSTS

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Oxidative conversion of propane-butane mixture by air to oxygen-containing compounds at T = 573-873 K and space velocity 330-15000 ч$^{-1}$ on polyoxide catalysts containing 1-10 % Mo, Ga, Cr of different composition and ratio supported on natural Torgai clays (TC), Sary-Ozek, Chankanai, IK-30 and IR-301 zeolites.

The experiments were carried out at atmospheric pressure in a continuous-flow unit with a fixed-bed quartz-tube reactor. Analysis of the reactants and products was carried out chromatographically with an "Agilent Technologies 6890N" instrument. The catalysts were investigated by X-ray diffraction (XRD), electronic microscopy (EM), infra-red spectroscopy, and their surface area, porosity, and elemental composition were determined.

Supported polyoxide catalysts on the basis of Mo, Cr, Ga, Bi, and Ce as well as natural clays of Kazakhstan, were tested in the process of oxidative conversion of propane-butane mixture. The influence of reaction temperature, contact time, composition and content of active component of catalyst were determined.

The gas mixture used for oxidation contained from 6,6 to 80,0 % C_3H_8-C_4H_{10} mixture and from 7,0 to 20,0 % oxygen in different ratios at 523-873 K and W = 300-15000 h^{-1}.

The treatment of sorbents with 10 % HCl facilitated the development of pores and an increase in the pore radius. The SiO_2/Al_2O_3 ratio (silica modulus) was increased after acid treatment too.

It was found that the partial oxidation of propane-butane mixture with varying the catalytic mixture composition and the contact time yielded acetone, methyl ethyl ketone, methanol, acetaldehyde, crotonic aldehyde, butanol, and acetic acid, as well as C_2-C_3 unsaturated hydrocarbons. It was shown that conversion proceeds with the formation of gaseous and liquid products. Important petrochemicals, such as acetone (773-823 K) and acetaldehyde (623-673 K) are main liquid products. Ethylene is the main product of gas phase. Yield of ethylene increases beginning from 723 K.

The investigation on influence of the nature of carrier on yield of acetone from reaction temperature was carried out. It was shown that more high yields of acetone were produced over Torgai white clay (TWC).

Mo, Cr and Ga samples show more optimal properties during investigation of the series of monometallic (Mo, Ce, Bi, Cr, Ga, Fe, Mn, Ni, Co and Zn) supported over TWC catalysts.

Ternary catalyst is more active than two-component samples. Optimal space velocities for catalysts with different content of active phase over carriers were determined. Up to 50,9 % of acetone and 38,0 % of methyl ethyl ketone on 5 % MoCrGa/TC were produced at $W = 450\ h^{-1}$. Increase of content of methyl ethyl ketone in catalysate was observed at reduction of propane-butane in reaction mixture. The determination of the product composition showed that the process follows a complex mechanism including oxidation, oxidative dehydrogenation, and cracking.

The optimal conditions for synthesis of products were detected:

- 50,9 % of acetone was produced on 5 % MoCrGa/TWC catalyst at 823 K and $W = 450\ h^{-1}$ in reaction mixture C_3-C_4:O_2:N_2:Ar = 5:1:4:5;
- 41,0 % of acetaldehyde was produced on 10 % MoCrGa/TWC catalyst at 723 K and $W = 450\ h^{-1}$ in reaction mixture C_3-C_4:O_2:N_2:Ar = 5:1:4:5;
- 80,0 % of methyl ethyl ketone was produced on 5 % MoCrGa/TWC + ZSM-5 + $Al_n(OH)_{3n-1}NO_3$ catalyst at 723 K and $W = 3150\ h^{-1}$ in reaction mixture C_3-C_4:O_2:N_2:Ar = 1:1:4:1;
- 71,4 % of ethylene was produced on 1 % MoCrGa/TWC catalyst at 723 K and $W = 450\ h^{-1}$ in reaction mixture C_3-C_4:O_2:N_2:Ar = 5:1:4:5;
- 83,0 % of benzene was produced on 1 % MoCrGa/TWC catalyst at 823 K and $W = 750\ h^{-1}$ in reaction mixture C_3-C_4:O_2:N_2 = 7:1:4.

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THERMAL IGNITION OF A HETEROGENEOUS SYSTEM IN A STIRRING SEMI-BATCH REACTOR

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The thermal ignition of a heterogeneous two-phase system of two immiscible liquids in a stirring semi-batch reactor was modeled. According to the accepted model at the initial time, a semi-batch reactor was filled with a solution of substance A. Then, a solution of substance B was supplied at the space velocity q to the point t_s in time, which corresponds to reaching an equimolar ratio between substances A and B in the heterogeneous system. Thereafter, the supply was stopped. As a result of mixing, the solution of substance B was dispersed and distributed as drops in the solution of substance A; for simplicity, these drops were considered adequate to spherical particles. The phase of substance A (a continuous phase) extracted substance B from the phase of substance B (a disperse phase). Extracted phase B is designated as B_A. The exothermal bimolecular reaction $A + B_A \rightarrow$ *products* occurs between reactants A and B_A. The heat exchange of the reactor with the environment occurs at the bottom and at the side face of the reactor. The model takes into account an increase in the lateral area of heat exchange during the supply of the solution of substance B, and interphase heat exchange is considered. Thus, the process in a semi-batch reactor is described by two macroscopic stages. At the first stage, the reaction occurs on the supply of the solution of substance B; at the second stage, it occurs after its termination.

The kinetic dependences of reactant concentrations, the dynamics of reactor heating, and the critical conditions of thermal ignition were studied. It was found that the initial temperature of the reactor had a considerable effect on its dynamic behavior.

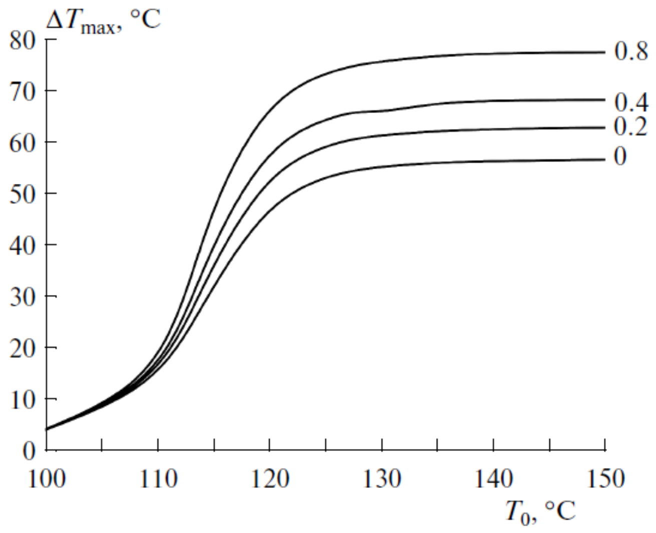

Fig. 1. Dependence of maximum heating on ambient temperature at $\beta = 10^{-3}$, $\varepsilon = 0{,}3$, $q = 0{,}6$, and $d_{max} = 1{,}0$. Here β is mass exchange coefficient (dm/s), ε is the distribution coefficient (a ratio between the concentrations of substance *B* outside and inside a drop at the interface), *q* is a mentioned above the space velocity of substance *B*, d_{max} is maximal diameter of a drop. Numbers in the graph correspond to values of θ

Figure 1 shows the dependences of the maximum heating ΔT_{max} on the ambient temperature T_0 for different values of the parameter θ (θ is a quantitative measure of polydispersivity; at $\theta = 0$ a system is monodispersive). From the data given in Fig. 1, it follows that the maximum heating ΔT_{max} increases with the parameter θ. This is natural because an increase in the interface surface area facilitates an increase in the rate of supply of reactant *B* into the phase of the solution of substance *A*.

As for the critical temperature, as it is well known from the theory of Semenov, it corresponds to a sharp change in the reaction regime from slow to explosive. This sharp change is caused by the fact that the theory of Semenov does not take into account burnout. However, if burnout occurs, a change from slow to rapid reaction is eroded, as can be seen in Fig. 1. In this case, it is reasonable to take the temperature corresponding to a curve knee in the coordinates of Fig. 1 as a critical temperature.

We found that the critical temperature for the model of the thermal ignition of the heterogeneous system in a semi-batch reactor at $\theta < 1$ varied in a very narrow range (106-108 °C at the chosen parameters). Therefore, for evaluating the safe operating conditions of the semi-batch reactor, it can be taken constant as an arithmetic mean value.

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HYDROGENOLYSIS OF 5-HYDROXYMETHYLFURFURAL TO PRODUCE 2,5-DIMETHYLFURAN OVER COMMERCIAL COPPER CHROMITE CATALYST

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1. Introduction

According to the literature [1-3], the biorefinery can be a good alternative to cover the current needs of energy, fine chemicals and unconventional fuels. 5-hydroxymethylfurfural (HMF) is considered one of the most promising intermediate for the 2,5-dimethylfuran (DMF) synthesis. DMF is particularly attractive because of its characteristics are similar to the gasoline ones. Recent literature [1-3] about DMF production reports that this biofuel/bioadditive can be produced in autoclave type reactor by heterogeneous catalytic hydrogenolysis of synthetic HMF using non-noble and noble metal catalysts. Taking this into account, this novel work is focused in catalytic hydrogenolysis of real and synthetic HMF using a fixed bed catalytic reactor.

2. Materials and Methods

Two feeds were used in experimental tests named “real” (obtained from fructose dehydration) and “synthetic” HMF (commercial). Feeds were composed of a mixture of 0.7 wt % of HMF in 1-butanol. The gas phase hydrogenolysis of the feeds was carried out in a continuous bench-scale fixed bed reactor, in which 0.2 and 0.5 g of commercial Cu/CrO_2 catalyst was diluted with inert SiC (catalyst/SiC = 1:9 wt). The catalyst was pretreated (673 K and 100 mL/min of pure H_2) and non-pretreated before reaction. Reaction was conducted for 4 h under a feed flow of 0.1 mL/min at temperatures of 473 and 498 K, and pressures from 0.5 to 3 MPa of H_2.

3. Results and Discussion

3.1. *“Real” HMF*

The preliminary activity tests were performed with pretreated and non-pretreated Cu/CrO_2 catalyst and “real” HMF feed at 473 and 498 K, 0.5 and 1.5 MPa, and WHSV of 0.15 h^{-1} (0.2 g of catalyst). The experimental results suggested that i) the catalyst pretreatment had a strong influence on conversion, specially on DMF yield, achieving a higher selectivity DMF with the non-pretreated catalyst, ii) the increase of temperature did not have strong influence on HMF conversion and DMF yield and iii) impurities of “real” HMF could have influenced the DMF selectivity.

3.2. “Synthetic” HMF

Taking into account the lowest selectivity obtained toward DMF, it was decided: i) to use “synthetic” HMF as a feed in order to eliminate the influence of “real” HMF impurities and ii) to increase the pressure from 0.5 to 3.0 MPa, maintaining the temperature at 473 K and WHSV = 0.15 h^{-1}. The obtained results (see Figure 1) compared with the corresponding results of “real” feed indicate that the DMF yield increased when the feed without impurities is used. Moreover, the increase of pressure improved the DMF yield, reaching similar values at 1.5 and 3.0 MPa. After analyzing these results, it was reduced WHSV from 0.15 to 0.06 h^{-1} (0.5 g of catalyst). The results presented in Figure 2 indicate that the WHSV reduction enhanced significantly the DMF yield when compared with the data showed in Figure 1. DMF yield increased especially when pressure was increased from 0.5 to 1.5 MPa, achieving a yield close to 60 %. Finally, the catalyst was tested at 473 K and 0.5 MPa (see Figure 2) and the results suggested that catalyst did not suffer an important deactivation because HMF conversion and DMF yield remained almost constant at the beginning and the end of the catalytic activity test.

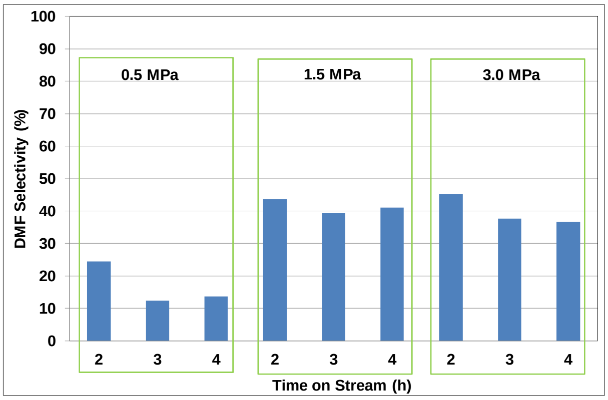

Figure 1. Synthetic HMF conversion and DMF yield obtained at 473 K, WHSV= 0.15 h^{-1} and different pressures

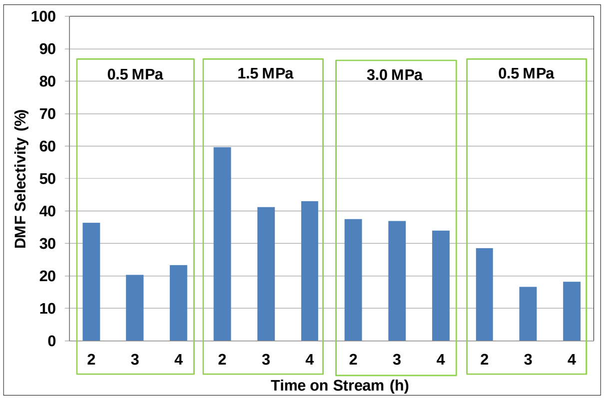

Figure 2. Synthetic HMF conversion and DMF yield obtained at 473 K, WHSV=0.06 h^{-1} and different pressures

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Acknowledgements

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PP-54

MEASUREMENT OF GAS-SOLID KINETIC RATE DATA FOR COMMERCIAL-SIZE FIXED-BED CATALYSTS USING A NOVEL JET LOOP REACTOR

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Introduction

Experimental reactors for measurement of reaction kinetics can be broadly classified according to the catalyst forms (powder, granule, or pellet) and the numbers of phases present (gas, gas-liquid, gas-liquid-liquid). It is generally agreed that for the purpose of generating kinetic data, laboratory-scale reactors that operate isothermally and allow direct evaluation of reactant conversions, product yields, and reaction rates from experimental measurements of flow rates and specie concentrations, such as that provided by devices where the fluid flow patterns approach perfect back-mixing, are preferred for various practical reasons over those where the flow patterns approach perfect plug flow [1,2]. Among various designs with nearly perfect fluid back-mixing, recycle reactors are preferred as important tools for catalyst testing and kinetic studies. Recycle reactors are also useful for the study of most commercially important reactions, although some exceptions occur, especially for cases where the catalyst activity changes rapidly when compared to typical fluid residence times. Some examples of various recycle reactor designs that have appeared in the open literature are illustrated in Figure 1a.

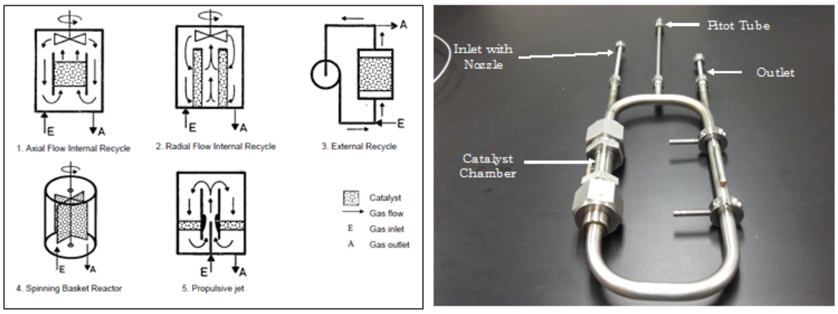

Figure 1a. Various types of recycle reactors;
Figure 1b. Photograph of a jet-loop reactor

The primary objective of this work is to describe the development, application and modeling of a new experimental reactor for studying the kinetics of gas-solid catalyzed reactions for commercial-size particles based upon the propulsive jet concept. This reactor can be broadly utilized for any fixed-bed gas-phase chemistry.

Materials and Methods

A photograph of the new reactor design is shown in Figure 1b. The one shown here is constructed of Type 316 stainless steel, although other materials of construction have been used. The catalyst chamber is sealed on both ends by Swagelok™ VCR fittings with metal gaskets for ease of installation. This design can accommodate several commercial size catalysts whose largest dimension is ca. 16 mm.

The test reaction used is the oxidation of SO_2 to SO_3 over V_2O_5-based catalysts. The reaction gases are mixed upstream and introduced at a steady flow rate from a gas manifold and removed through the outlet whose back-pressure is maintained constant by a back-pressure regulator. Analysis of SO_2, O_2 and N_2 in the feed and product gases is performed with an on-line GC. A pitot tube located on the return leg is used to measure the internal gas recirculation rate. A large number of experiments were conducted in which the total gas flow rate, gas temperature, reactor total pressure, catalyst particle size, nozzle size, and nozzle location were systematically varied to assess the effect of these variables on the gas recycle rate.

Results and Discussion

An example of typical kinetic data is provided in Figure 2. These data are based upon temperatures between 400 to 475 °C using a gas feed consisting of ca. 1 % SO_2, 7.5 % O_2 and 82.5 % (bal) N_2 at flow rates between 100 sccm to 900 sccm. The resulting rate data are fitted to a rate model that accounts for reversible reaction behavior, although more complex rate equations can be evaluated for goodness-of-fit using robust parameter estimation methods.

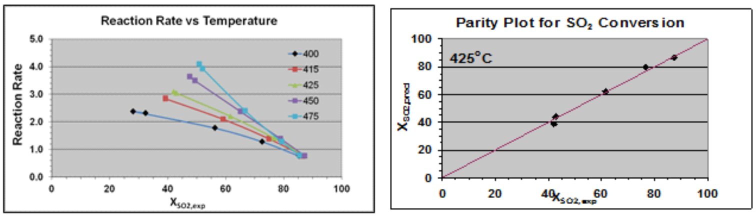

Figure 2a. Reaction rate vs. Temperature;
Figure 2b. % SO_2 conversion–exp vs. model.

The agreement between the reaction rates *vs* % SO_2 conversion data is shown below in Figure 2a. A parity plot (Figure 2b) shows a comparison between the experimental and model-predicted % SO_2 conversions at a selected temperature (425 °C). Good agreement is obtained, which illustrates the validity of a simple but effective reaction rate model. These and other detailed results will be presented that demonstrate the utility of the proposed jet loop reactor as a relatively simple but effective reactor type for studying the kinetics of gas-solid catalyzed reactions having either fundamental importance or commercial application.

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PP-55

ANALYSIS OF TRANSPORT-KINETIC INTERACTIONS FOR SO_2 OXIDATION IN PARTICULATE AND MONOLITH H_2SO_4 CATALYSTS

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Introduction

Development of next-generation chemical processes that have zero emissions is a key environmental objective for sustainable development. The manufacture of H_2SO_4 by the air oxidation of SO_2 to SO_3 is an important technology where an opportunity exists for new catalyst development and process innovation by reducing emissions of unconverted SO_2 in process reactor tail gases. Emissions control technologies using front-of-pipe technology, such as new catalyst technology, improved reactor designs, and process operational strategies have greater potential to be more economical versus end-of-pipe scrubbing technologies.

From a catalyst design perspective, specification of catalyst composition, catalyst size, catalyst shape and internal pore structure are interlinked parameters that have received notable attention by catalyst scientists since these affect the catalyst effectiveness factor, bed pressure drop, rate of catalyst attrition, catalyst mechanical integrity, and catalyst life. Specification of catalyst design parameters requires optimization since tradeoffs exist in how catalyst performance may be affected by altering one or more of the above parameters.

The primary objective of this study is three-fold: (1) to review the current state-of-the art in modeling transport-kinetic interactions for catalysts utilized in the oxidation of SO_2 to SO_3; (2) to evaluate monolith catalysts as potential candidates as SO_2 oxidation catalysts; and (3) to develop modeling framework to compare reactor designs for both particulate and monolith catalysts under typical multi-pass convertor operation with potential for process optimization.

Methods

Catalyst shapes that have been proposed for SO_2 oxidation to SO_3 include multiple lobes, hollow rings and cylindrical shapes. In the case of catalyst shapes involving multiple lobes, the shape parameters include the number and shape function of the lobes, the characteristic dimension of each lobe, the distance from the lobe center to true particle center, and the diameter of the hollow center region.

COMSOL Multiphysics is used to model non-isothermal diffusion, reaction and transport effects with compositional and temperature dependence of all model parameters, which builds upon our previous work [1]. A new model that describes transport-kinetic interactions in monolith catalysts is described that is valid for process conditions encountered in multi-pass convertor operation. Additional multiphysics for the monolith catalyst model include the Brinkman equation to describe convective transport in the monolith catalyst layers. The reaction kinetic model is based upon the work of Collina *et al.* [2] since it accounts for the dependence of the SO_2 oxidation rate on the partial pressures of SO_2, O_2, and SO_3 with inhibition by both SO_2 and SO_3 from 450 to 590 °C. Concentration and temperature profiles were compared using various diffusion flux models (Wilke, Wilke-Bosanquet, Maxwell-Stefan, and Dusty Gas) over conditions used for multi-pass convertor operation.

Preliminary Results and Discussion

Typical SO_2, O_2, and SO_3 concentration profiles for particulate and monolith are shown in Figure 1. Here, the Wilke model is used to describe the diffusional fluxes. The particle surface or the catalyst layer is exposed to a constant bulk concentration or temperature. The particle-scale model provides the starting basis for coupling local particle behavior to the external particle field equations, which is essential component of SO_2 oxidation reactor modeling.

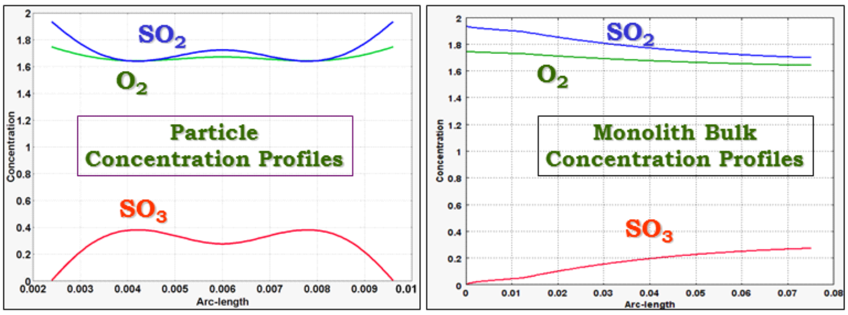

Figure 1. Concentration profiles for particulate and monolith catalysts

Additional results that compare the performance of particulate versus monolithic catalyst shapes using typical process conditions will be presented and discussed, thereby showing the incentive for development of monolithic catalyst with higher activity and reduced emissions.

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PP-56

THE EFFECT OF NON-SPHERICAL CATALYST PARTICLE SHAPES IN GAS PHASE FISCHER-TROPSCH SYNTHESIS

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The Fischer-Tropsch Synthesis (FTS) is a highly exothermic condensation polymerization reaction of syngas ($CO+H_2$) that occurs in the presence of supported Fe/Co/Ru-based catalysts to produce a wide range of paraffins, olefins and oxygenates, the latter of which is often called *syncrude*. Multi-Tubular Fixed Bed Reactors and Slurry Bubble Column reactors are widely employed for FTS processes [1]. To understand the reactor-scale catalyst performance, it is important to first analyze particle-scale transport-kinetic interactions. The FTS reaction network produces hydrocarbons with carbon numbers typically ranging from 1 to 100 so the catalyst pores in this process can be potentially filled with liquid wax (C_{20}+) leading to high diffusional limitations. To model such a reaction network and account for all species, micro-kinetic rate expressions for each individual species must be coupled with the intraparticle solubility of gases in liquid wax and transport equations for the various reaction species in the porous catalyst.

A 2-D particle model for different catalyst shapes (solid cylinder, hollow cylinder, 4-hole cylinder, modified 4-hole cylinder and 7-hole cylinder; see Figure 1) was numerically simulated using COMSOL Multiphysics™ to compare the particle-level performance. Previous work only considered spherical catalysts. The dimensions of the various catalyst particle shapes are given in Table 1. The Fe-based micro-kinetic olefin re-adsorption model developed by Wang *et al*. (2008) was coupled with the Soave-Redlich-Kwong equation of state to describe the particle-scale transport-kinetic interactions and phase behavior for the gas-phase FTS [4]. A total number of 20 paraffins (C_1 to C_{20}), 19 olefins (C_2 to C_{20}) and 4 key components (H_2, CO, CO_2, and H_2O) are considered in the reaction network, which leads to a system of 43 second-order nonlinear, coupled differential equations for the specie mass balances. The micro-kinetic and thermodynamic expressions used in the model can be found elsewhere [3-5]. The intra-particle effectiveness factor, liquid-to-vapor ratio, CO conversion and intra-particle volume-averaged concentration of diesel were evaluated at different process conditions to compare the performance of the different catalyst particle shapes.

The intra-particle concentration profiles in the diesel range (C_{13}-C_{17}) for different catalyst particle shapes for isothermal conditions are shown in Figure 2. The results show that the volume-averaged diesel concentration (mol/m^3) in the hollow cylinder is similar to that of the solid cylinder, which suggests that the selectivity of the catalyst can be maintained while reducing the material in the catalyst pellet.

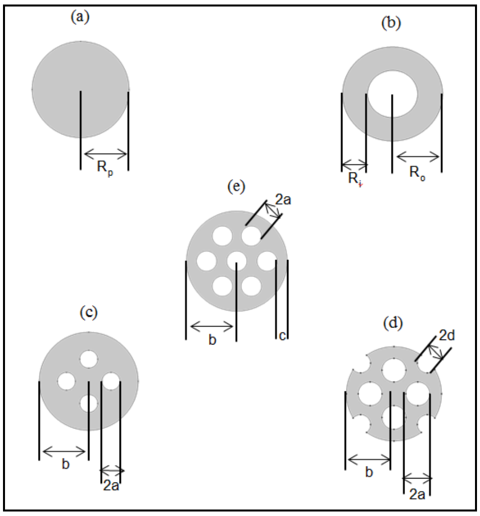

Figure 1. Catalyst particle shapes. (a) cylinder, (b) hollow cylinder (H-Cylinder), (c) 4-hole cylinder (4-H Ring), (d) modified 4-hole cylinder (M-4-H Ring), and (e) 7-hole cylinder (7-H Ring)

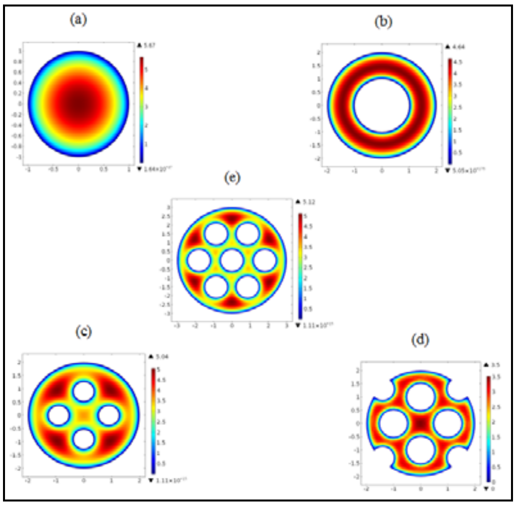

Figure 2. Intra-particle concentration profiles of diesel (mol/m^3) at T = 493 K and P = 25 bar. (a) cylinder, (b) hollow cylinder (H-Cylinder), (c) 4-hole cylinder (4-H Ring), (d) modified 4-hole cylinder (M-4-H Ring), and (e) 7-hole cylinder (7-H Ring)

Table 1. Dimensions of various catalyst particle shapes with equal characteristic diffusion length based on the equivalent diameter of a sphere

Cylinder	L = 3 mm & R = 1 mm
H-Cylinder	L = 3 mm, R_o = 2 mm & R_i = 1 mm
4-H Ring	L = 3 mm, b = 2 mm, a = 0.36 mm & c = 0.54 mm
M-4-H Ring	L = 6 mm, b = 2 mm, a = 0.5 mm, c = 0.5 mm & d = 0.415 mm
7-H Ring	L = 6 mm, b = 3 mm, a = 0.6 mm & c = 0.6 mm

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PP-57

MATHEMATICAL MODELLING OF CATALYTIC CRACKING RISER REACTOR

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Development of the oil refining industry is characterized by the commitment to increase of the production capacity of the destructive and enriching processes and light oil products and decrease of the residual oil production. At the same time, catalytic cracking and hydrocracking are the most advanced destructive secondary catalytic processes of Russian oil refining industry.

Optimization of the light oil production from heavy oil fractions can be possible with using the strategy of the system analysis and the method of kinetic and thermodynamic modelling [1-2]. Mathematical model of catalytic cracking was developed. Formalized hydrocarbon conversion scheme of catalytic cracking was the basis for the development of the catalytic cracking mathematical model. The kinetic equations describe the change in concentration of the reactants depending on contact time with the initial conditions: $\tau = 0$, $C_i = C_{i0}$, where i is the corresponding hydrocarbon [3].

Heat balance of catalytic cracking riser and amount of coke on the catalyst surface depend on the hydrocarbon composition of feedstock, temperature and activity of the catalyst after regeneration stage in a greater degree. Dynamics of coke accumulation determines the quantity of coke combustion during the regeneration and temperature of circulating catalyst and therefore, the process temperature, composition and yield of the light fractions from a catalytic cracking unit.

Kinetic model equations were supplemented by heat balance equations taking into account the heat transfer between the gas and catalyst and thermal effects of main catalytic cracking reactions with the initial conditions $T_{g,c} = T_r$, $l = 0$:

$$\omega_g \rho_g c_g \frac{dT_g}{dl} = \alpha a_v (T_c - T_g)$$

$$\omega_c \rho_c c_c \frac{dT_c}{dl} = \alpha a_v (T_g - T_c) - \sum_{i=1}^{n} (\Delta \mathrm{H}_i \, \omega_i) \qquad (1)$$

where T_r – temperature equilibrium between gas, water steam and catalyst; ω, ρ, c – velocity, density and heat capacity of gas or catalyst, m/s, kg/m^3, kcal/kgK;

$T_{g,c}$ – temperature of gas or catalyst, K; α – heat-transfer coefficient taking into account temperature gradient in the catalyst particles, kcal/m^2·s·K; a_v – specific surface area of heat transfer, m^2/m^3; ΔH_i – thermal effects of the i-th component chemical reaction, kcal/kg; ω_i – chemical reaction rate, mol/ m^3·s.

Prediction the process temperature, composition and yields of the light fractions, octane number of gasoline depending on the catalyst temperature after regeneration stage, feedstock composition and catalyst : feedstock ratio can be possible with using developed mathematical model.

According to calculations, dependence of the process temperature on the catalyst temperature after regeneration stage (fig. 1) was defined at refining of vacuum distillate with high concentration of paraffin and naphthenic fraction (65.8 % wt). It was defined that to achieve the maximum yield of gasoline fraction it is necessary to maintain the process temperature at 530 °C, catalyst : feedstock ratio at 5.9 : 1, at that the coke yield will be 4.5 % wt.

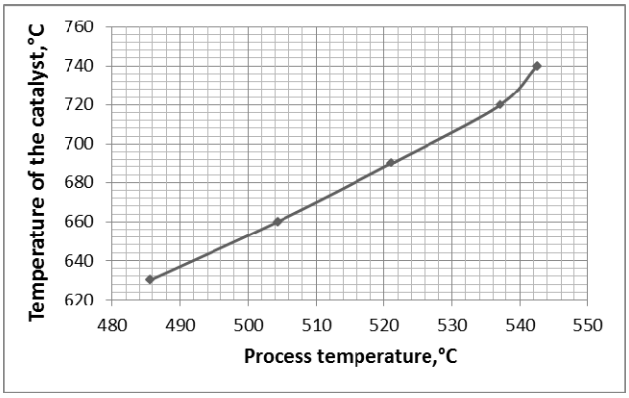

Figure 1 – Dependence of the process temperature on catalyst temperature

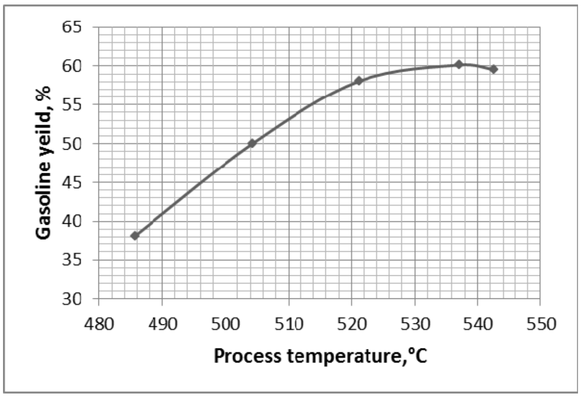

Figure 2 – Dependence of the gasoline yield on the process temperature

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PP-58

COMPARATIVE STUDY OF CONVENTIONAL, REACTIVE-DISTILLATION AND PERVAPORATION INTEGRATED HYBRID PROCESS FOR ETHYL TERT-BUTYL ETHER PRODUCTION

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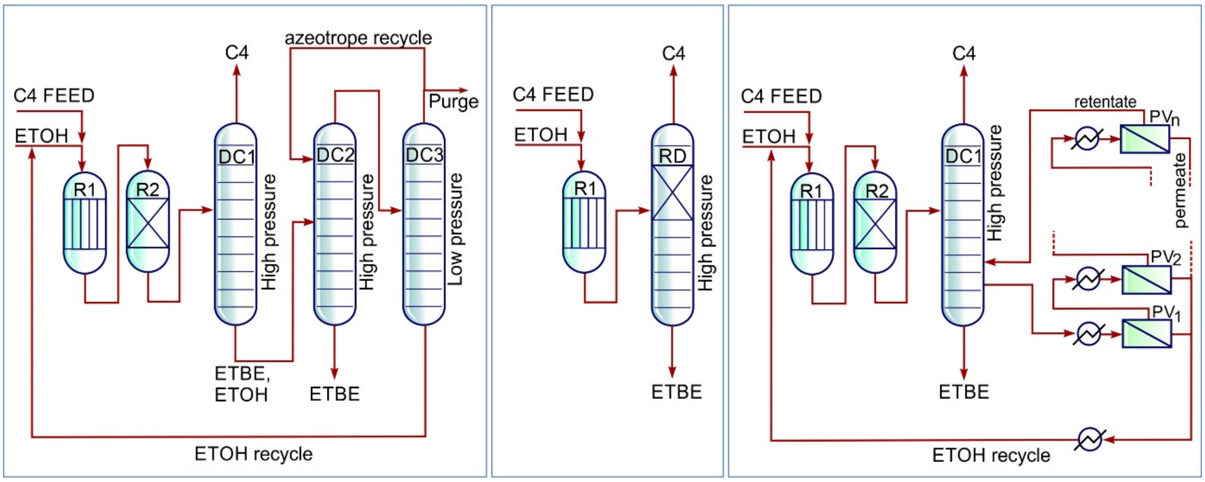
The aim of this work is to simulate and numerical comparison of different processes for the production of ethyl-tertiary-butyl-ether (ETBE) using Aspen Plus (AP) and Aspen Custom Modeler (ACM) software. ETBE have been being used as an oxygenate gasoline additive in the production of gasoline from crude oil [2]. In conventional production, the separation of alcohol-ether mixtures occurs by distillation, which is based on the change of ethanol/ETBE azeotropic composition with pressure. The feasibility of conventional distillation process with three distillation column (base case) [3], reactive distillation combined with pre-reactor [4] and pervaporation integrated hybrid process for ETBE production [5] are researched and examined by simulation in AP (Figure 1).



a) b) c)

Figure 1. a) Conventional; b) Reactive Distillation combined with pre-reactor; c) PV integrated Hybrid process for ETBE production. R-Reactor, DC-Distillation column, RD-Reactive Distillation column, PV-Pervaporation unit

Calculation of vapor liquid equilibrium of C4/ETBE/Ethanol system is done using UNIFAC model. A methodology for the study and selection optimal parameters for reaction system, distillation column and membrane modules is analyzed. The feed and recycle stages, number of stages, reboiler duty, reflux ratio for distillation column are determined and their effects to the separation, energy consumption and CO_2 emission in the process are studied.

Table 1. Simulation results for the ETBE production processes

Process	ETBE product (kg/hr)	Total Utilities (MW)	CO_2 emission (kg/hr)
Conventional	6703	12,62	2728
Reactive Distillation	6983	20,32	4546
Hybrid process	6733	8,25	1768

The overall scheme of conversion in the synthesis of ETBE can be represented as:

$$iC_4 + Ethanol + nC_4 \overset{\square}{\leftrightarrow} ETBE + nC_4$$

$$iC_4 + H_2O \overset{\square}{\leftrightarrow} TBA$$

The model of the industrial reactors and distillation columns are developed by using a stoichiometric reactor RSTOIC and a rigorous distillation model RADFRAC respectively. A simulation model of a membrane unit is developed in ACM and implemented in AP to investigate the representation of a PV integrated hybrid process. PERVAP2256 membrane results are used for the simulation of membrane module [1, 6]. We have concluded that the hybrid process is more economical in consumption of utilities and it shows lower CO_2 emission than other processes those of studied in this paper.

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Acknowledgements

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PP-59

MULTI-PHASE MODELING OF NON-ISOTHERMAL REACTIVE FLOW IN FLUIDIZED BED REACTORS

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We investigate a model fluidized bed reactor where a highly concentrated solution of liquid formic acid (FA) is decomposed to a gaseous mixture of carbon dioxide (CO_2) and Hydrogen (H_2) in the presence of microscopic floating solid catalytic particles (Cat). We describe the system, contained in a fixed control volume, as a mixture composed of the 9 constituents together with 5 phase change mechanisms. For the individual mixture components, we distinguish partial densities and momenta, while we only consider one common temperature field for the mixture as a whole. The system is, under certain assumptions, reduced to a three (pseudo-) phase system. Assuming a perfect mixing of the catalytic solid particles, which was observed in the experiment, the system can be treated as two phase flow.

The liquid mixture phase is considered as a compressible viscous fluid with temperature-dependent density and viscosity depending on both the temperature (Arrhenius model) and the volume fraction of the catalyst particles. Physical interaction between the gaseous mixture phase (bubbles) and the liquid is modelled by the pressure-drag balance. The chemical rates satisfy the mass-action law and follow the Arrhenius kinetics.

In addition to inner reactor body simulation, we model also the heating system which is composed of several hollow metal tubes heated by passing oil flow driven by thermostat pump.

The model was implemented numerically in COMSOL Multiphysics and we present several simulations and optimization results addressing primarily the role heating body design, distribution and latent power.

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PP-60

GREEN ETHYLENE CATALYTIC PRODUCTION FROM OAT HULLS ALCOHOL AND ITS DOWNSTREAM CONDITIONING

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Resent progress in synthesis of highly valuable PE-carbon nanotubes composite materials has stimulated search for small-scale ethylene production from renewable non-edible resources. Lignocellulosic biomasses, such as wheat straw, oat hulls and other agricultural residues are attractive materials for bioethanol (bioEtOH) production, due to its worldwide availability and low cost. Generally, the bioEtOH-based "green" C_2H_4 can be produced in four steps: biomass fermentation to a crude bioEtOH; rectification to purify the EtOH; catalytic dehydration of EtOH; treatment of the crude C_2H_4 and production of the target-grade C_2H_4. Results of catalytic conversion of crude and purified bioEtOH on specially designed and prepared alumina catalysts, followed by conditioning of the crude C_2H_4 to the grade appropriate for synthesis of functional polymer-nanocarbon composites are discussed in this paper. The crude bioEtOH that was synthesized from oat hulls in IPCET SB RAS (Russia, Biysk) had been rectified and used in the dehydration process as 96 % bioEtOH. On an anhydrous EtOH, mass concentration of organic impurities in bioEtOH was 0.02-11 g/L, primarily as acetaldehyde and propanol. If their content is more than 0.02 g/L, this reduces selectivity to C_2H_4 in bioEtOH dehydration, and subsequently, increases content of oxygenates in the crude C_2H_4 which complicates C_2H_4 conditioning. In ethylene intended for PE-based composite materials synthesis, the content of oxygen-containing substances should not exceed 6.5…700 ppm. Among them, CO and H_2O contents are the most strictly limited, to 1…50 ppm and 3…300 ppm, respectively. The crude ethylene produced on the pilot setup by catalytic dehydration of EtOH contained (mol. %, ave.): 45 % C_2H_4, 53 % H_2O, 1.4 % oxygenates (aldehydes, ethers, alcohols), 0.3 % alkenes and H_2, 0.1 % olefins, and 0.03 % COx. For downstream conditioning of C_2H_4, water condensation at 283 K, cryogenic cooling at 270-233 K, catalytic CO oxidation and final adsorption of H_2O, VOCs and CO_2 have been used. Catalytic dehydration process, in conjunction with downstream ethylene conditioning was studied; the optimal operation conditions for C_2H_4 production of the target quality were developed.

Acknowledgements

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PREPARATION AND HYDRODESULFURIZATION PERFORMANCE OF B-PROMOTED ALUMINA-SUPPORTED Co-Mo SULFIDE CATALYSTS

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In recent years, R&D of hydrodesulfurization (HDS) catalysts to produce low-sulfur fuels has been one of the principal issues in the petroleum industry due to the increasingly strict environmental requirements. Different approaches on the optimization of HDS catalysts have been focused on the modification of transition bimetal sulfides to improve HDS performance. It was well known that the active compound of the supported HDS catalyst is mainly composed of Mo sulfide promoted by Co or Ni on alumina because of their high selectivity and activity [1]. To obtain much more effective catalyst boron can be used as a promoter with high activity, selectivity and stability. It has been reported that the incorporation of boron modifies the dispersion of Mo and increases the selectivity and the strength of the acid sites of the bulk catalyst [2]. In this work, a series of γ-alumina supported CoMo catalysts promoted by boron loadings (1-5 wt %) were synthesized by incipient to wetness impregnation method. The catalytic experiments were evaluated in a fixed-bed reactor loaded with 16 ml catalyst diluted with SiC particles using feedstock (diesel) with the sulfur content of 6100 ppm. Reactor operating conditions were kept at 70 bar and 350 °C. Before the reaction the catalyst was presulfided to enhance the catalytic activity. The reaction is carried out in the presence of hydrogen to remove sulfur from hydrocarbon molecules. For the analysis of the total content of sulfur the liquid product was collected after 6 hours at steady state conditions. The effect of boron loading sequence and percentage were observed by the comparison of HDS activity over each prepared catalyst. Simulated distillation (simdis) by gas chromatography is used to analyze the composition and sulfur content of the product stream. It is important for a catalyst to remove sulfur and keep the diesel component in product stream.

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LOW-TONNAGE PRODUCTION OF ORGANIC COMPOUNDS

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Basic industries use a wide range of chemical products, obtained on the basis of deep technological modifications and fine organic synthesis.

Boreskov Institute of Catalysis, Siberian Branch of RAS (BIC SB RAS) has experience in developing technologies to produce of fine chemical products: organic acids and their derivatives; a series of aromatic compounds; rubber chemicals; plasticizers and various additives for making of special compositions; glues; polymers and other materials with desired properties [1, 2]. The development of novel catalytic methods of organic compounds synthesis is carried out with using the last generation of catalysts, in particular $Q_3\{PO_4[WO(O_2)_2]_4\}$, where Q^+–organic cation [3], modified non-Keggin, high vanadium aqueous solutions of gross composition $H_aP_zMo_yV_xO_b$ [4], 0.2-0.5 % Pd/Sibunite, zeolite H-BETA and etc.

Realization of new technologies is carried out on working areas of the Volgograd Department of BIC SB RAS. Integrated approach applies for the organization of manufacture, including flexible chemical-engineering schemes (HTS) and microreactor technologies too.

It should be borne in mind that the development of new production processes for organic compounds using conventional approaches requires scaling-up of the method developed at the laboratory level. This requires additional process optimization at every scaling stage. This way of technology transfer from laboratory to industry is often not only expensive but also time- and labour-consuming. Of course, many problems of reactor scaling up can be solved by mathematical modelling. However, for the industrial synthesis of compounds in small amounts, the scaling up problem could be solved (Fig.1) using particularly microchannel systems (MCR); in this case, process development and its optimization can be carried out in laboratory in a single reactor [5], as the increase in the production capacity can be attained by merely increasing the number of MCR used [6, 7].

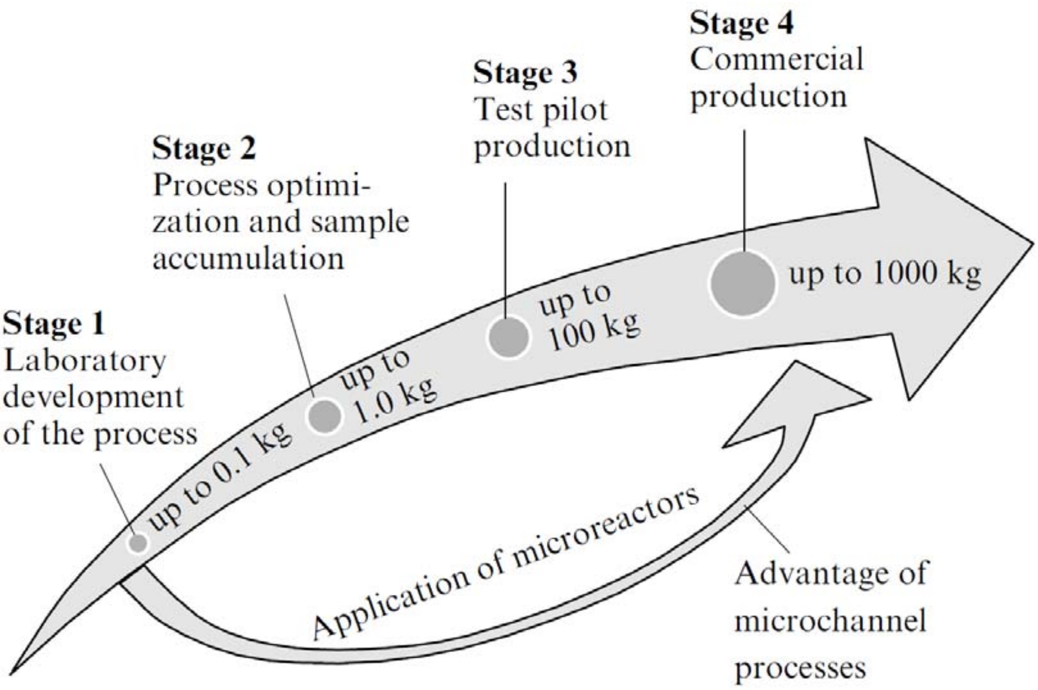

Fig. 1. Sequence of the design of small-scale chemical processes in the conventional approach and with the use of microchannel reactors

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DESIGN OF THE MODULAR FISCHER-TROPSCH SYNTHESIS REACTOR USING CFD MODELING

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A compact modular multichannel reactor with microchannel heat exchangers installed between catalytic bed channels (Fig. 1) was developed in our previous work [1], and since then, the size of the module has been increased with additional catalytic beds and coolant channels for the purpose of minimizing the capital cost. In the present study, A computational fluid dynamics (CFD) model for the module was considered to evaluate the effects of the size of the catalytic bed on the thermal behavior of the reactor in such a way the optimal size was suggested in the sense of both maximum productivity and thermal stability. Detailed levels of mass, heat and momentum balances were considered, and FTS reaction rates for lumped hydrocarbon distributions (C_1, C_{2-4}, and C_{5+}) were determined. The validity of the proposed model was corroborated by comparing simulated results with experimental data under a variety of operating conditions. The cooling performance of the microchannel cooling system was shown to be satisfactory despite high heat release rate, resulting in negligible temperature gradient along the catalytic beds. The model was used to investigate the temperature profiles in the catalytic beds as well as the phase of cooling media in the microchannel cooling system with varying fraction of inert materials and space velocity to investigate the cooling performance of microchannel heat exchangers. Simulation results showed that, even when no inert materials were used in the catalytic bed, the latent heat of water in the cooling channels was enough to maintain the temperature increase less than 20 K for all the catalytic beds in the system, preventing a possible thermal runaway. In addition, the thermal behavior was analyzed when the height of the catalytic bed was increased while the number and size of coolant channels were maintained. It was observed that the peak temperature was increased by up to 30 K which was considered to be acceptable temperature rise. In conclusion, the developed model was proven to be a useful tool for the design of microchannel based FTS reaction system.

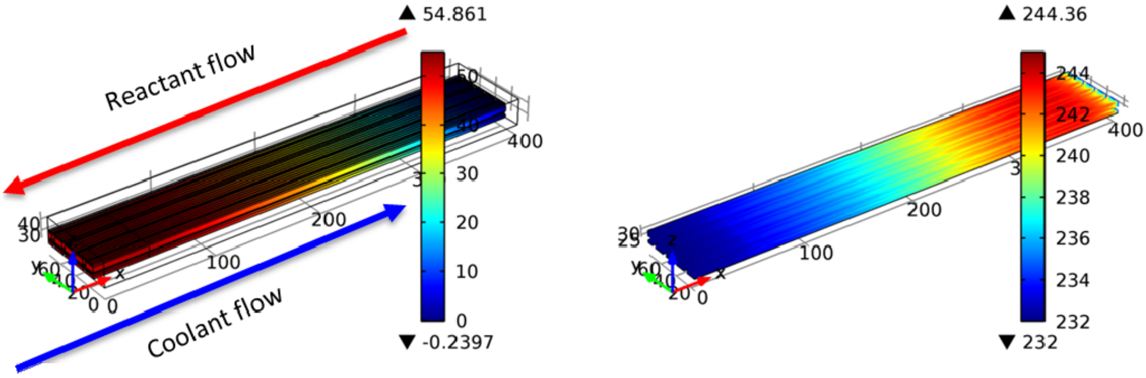

Figure 1. Profiles of CO conversion (left) and temperature (right) in the catalytic bed of a modular multichannel FTS reaction system; space velocity = 9,287 mL/(g_{cat}·h), feed temperature = 505 K, pressure = 2.1 MPa.

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EFFECT OF CATALYST MACROSTRUCTURE ON RATES, RESIDENCE TIME AND MICRO-MIXING IN A PHOTOCATALYTIC SPINNING MESH DISC REACTOR

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The spinning mesh disc reactor (SMDR) is an extension to conventional spinning disc reactor (SDR) technology, where a mesh or grooved disc surface is used to expand the available catalyst surface area contacting the thin film of liquid reactant phase which is highly sheared on the surface of the rotating disc. Different flow regimes of highly sheared thin liquid films can form across the surface of the disc depending on the flow rate, rotational speed and liquid properties. It is the nature of these flow regimes that dictate the claimed advantage of spinning disc reactor technology – high mass and heat transfer [1-3]. The Patterson research group has applied SDR technology to photocatalytic reactions [1-3] and have found that under a narrow range of operating conditions, process intensification compared to a conventional annular flow photoreactor is possible [1]. A wider operating envelope achieving higher reaction rates/process intensification is desired, finding flow regimes that increase mixing to overcome the oxygen mass transfer rate limiting step at higher initial reactant concentrations [3]. We hypothesise that using mesh and textured discs (as per a SMDR) would be a solution to this, via the mesh/texture increasing the potential photocatalyst surface area on the disc, as well as improving mass transfer from enhanced micro-mixing in the thin liquid film on the disc compared to smooth discs.

Consequently the aim of this work was to determine the effect of using textured discs (meshes and grooves as a macrostructure) on reaction rate in a photocatalytic SMDR. The effect of rotating speed, disc macrostructure (meshes/grooves/smooth), oxidant input amount (oxygen added or not) and volumetric flowrate were investigated and related to four key reaction/reactor parameters: reaction rate (using photocatalytic degradation of a water soluble organic – methylene blue), hydrodynamics on the catalyst (by high speed photography of the liquid films), residence time distribution (measured by tracer analysis) and micro-mixing (measured by the Villermaux-Dushman reaction). The photocatalyst used was sol-gel coated on glass and steel (discs and meshes). Reaction rates (on a surface area basis) in the reactor were calculated via a mass balance and reactor modelling of the system (as per [2]).

Results demonstrated that reaction rate can be maximised through identification of the optimal spinning speed, disc surface structure (meshes/grooves/smooth), oxidant input and volumetric flowrate. Higher disc spinning speeds make the residence time distributions more plug flow in behaviour and increase micro-mixing, which is known to increase reaction rate. However an intermediate disc speed of 300 rpm at a 20 mL/s inlet flow for a mesh/textured disc with a square grooved pattern was found to give the highest reaction rate. Analysis shows that using a patterned/mesh disc is optimal, since it smooths out the surface flow across the disc, which both increases local UV penetration (less scattering) and provides more uniform volumetric utilisation of the catalyst. This effect appears to dominate the other positive effects of higher spinning speeds.

Overall this work shows that reactor and photocatalyst surface macrostructure and design plays an important role in maximising photocatalytic SMDR reaction rates. Moreover, the process intensification (higher reaction rates and photonic efficiency) and self-aeration facilitated by the open spinning disc surface, indicates that the photocatalytic SMDR is superior compared to conventional photocatalytic reactors [3]. To determine if this is more generally applicable to further types of reactions and reactors, the SMDR concept is currently being extended to non-photocatalytic reactions.

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GLYCOLYSIS REACTION KINETIC PARAMETERS EVALUATION

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Glycolysis reaction is typical enzyme reaction. In our study it was used as a case study for kinetic parameters estimation. Special attention was paid to the immobilization of enzyme glucose oxidase. It was immobilized with covalent bound to the silica gel with a particle size (0.063-0.2) mm. Process conditions were as follows: temperature, T = (25, 30, 35 and 40) °C, rotational frequency of the stirrer, f_{s} = (0, 150 and 300) min^{-1}, air flow rate, $q_{\mathrm{V,air}}$ = (0,10, 20 and 30) L/h and pH = (5, 6, 7 and 8). Experiments were performed in a thermostatically controlled laboratory batch reactor EasyMax 102. The concentration of glucose was determined using a spectrophotometer at 500 nm.

It is well known that enzyme stability and activity are strongly dependent on the substrate pH value. For this purpose, we carried out the glycolysis reaction first with the free enzyme in the pH range (6-7.5). The conversion was almost equal in all cases regardless of the substrate pH. Then, the reaction was performed at different substrate pH with immobilized enzyme. In this case the maximum conversion was reached at the pH = 6. Therefore, further reactions were all carried out at pH = 6.

The glycolysis reaction takes place in the presence of oxygen. Thus, we perform the reaction with purging the reaction medium with air. The conversion in the case without purging was relatively low; after 3 h only about 20 %. Conversion was increasing with increasing air flow rate until $q_{\mathrm{V,air}}$ = 20 L/h. At $q_{\mathrm{V,air}}$ = 30 L/h, the conversion was lower again, because the air bubbles caused sweeping of silica gel particles together with an immobilized enzyme from the reaction medium and they were sticking on the wall of the reactor.

Furthermore, we examined the effect of rotational frequency of the stirrer on the reaction efficiency. The highest conversion (96 %) was reached at f_{s} = 300 min^{-1}. Thus, we further investigated the influence of reaction temperature on the conversion at optimal pH, air flow rate, and rotational frequency of the stirrer. Obtained conversions at different temperatures are shown in Figure 1.

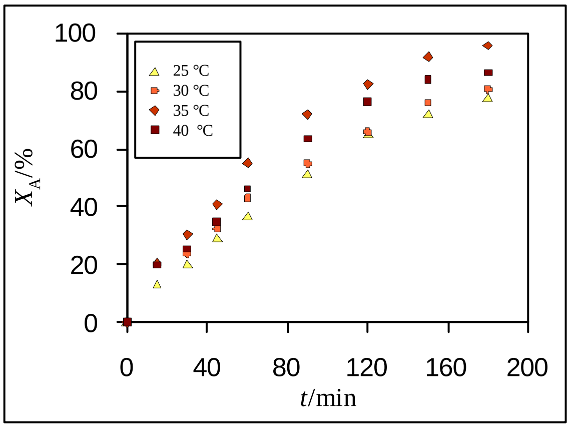

Figure 1. Conversion versus time at different temperatures and f_m = 300 min^{-1}, $q_{V,air}$ = 20 L/h and pH = 6

It is clear from Figure 1, that conversion increases with temperature and reaches its maximum at T = 35 °C. Further temperature increase resulted in slight conversion decrease. The reason is loss of activity due to denaturation of the enzyme at higher temperatures.

Repeated reactions with the same immobilized enzyme were also carried out with the aim of verifying the influence of enzyme deactivation on the conversion. It decreased for approximately 36 % after the second reaction, and for another 25 % after the third one. The difference was quite large, which is probably the consequence of enzyme deactivation or enzyme leaching from the support.

Finally, all previously measured process parameters enabled us to determine kinetics of the selected reaction. It was proven that enzymatic glycolysis reaction follows the simple Michaelis-Menten mechanism, with no inhibition effects. Thus, Michaelis-Menten constants, reaction rate constants, activation energy, and pre-exponential factor were successfully determined. All parameters are in the range of already published values for similar enzyme reactions.

KINETIC MODELLING OF THE TRANSFORMATION OF DME INTO OLEFINS ON A HZSM-5 ZEOLITE CATALYST

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The DTO (Dimethyl ether To Olefins) process is presented as an alternative to MTO process (Methanol to Olefins). The initiative aroused great interest due to the increasing availability of DME and the advantages of its production over that of methanol. The synthesis of DME is considered to be a better option to valorizate syngas than the Fischer Tropsch synthesis, in particular using lignocellulosic biomass feedstocks, what associated with the growing availability of natural gas [1] has good prospects for the industrial implementation of this process [2]. Although the technological development of the DTO process is in continuous growth leading to numerous studies [3,4], there is a scarce knowledge of the kinetic modelling of the process which is an interesting strategy for the design of the reactor and the regenerator with an industrial implementation point of view.

With the aim of gaining knowledge of the catalytic conversion of DME to olefins, this work contributes quantifying the effect of the reaction conditions (temperature, space time and partial pressure) on the product distribution in the DTO process using a kinetic model of lumps. The study has been carried out on a HZSM-5 zeolite catalyst with SiO_2/Al_2O_3=280 ratio agglomerated with boehmite as a binder, given that with this catalyst a suitable balance is stricken between activity, selectivity and stability, which is explained by the limited density and acid strength of the acid sites that hinder the secondary aromatization and hydrogen transfer reactions, as well as the olefin condensation reactions responsible for the coke formation.

Different kinetic models have been proposed and kinetic parameters of best fit for each kinetic model have been calculated by multivariable nonlinear regression using a program written in MATLAB®. The parameters optimized are the kinetic constants (at 350 °C, reference temperature) and the activation energies, and the optimization has been carried out by minimizing an objective function established as the sum of square residuals between the experimental and calculated values of composition. The values predicted by the models have been calculated using different routines for the integration of the mass balance for each lump. Figure 1 shows the kinetic scheme corresponding to the best fit to the results. The products have been grouped into the following lumps: CH_4; C_2H_4; C_3H_6; C_4H_8; C_2-C_4 paraffins; MeOH, DME; BTX; C_{5+} aliphatic fraction and CO+CO_2.

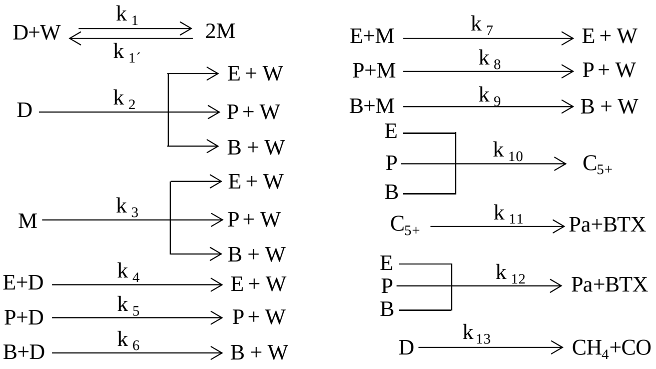

Figure 1. Kinetic scheme proposed

As an example of the goodness of fit, Figure 2 compares the experimental results (points) of each lump composition and those calculated using the kinetic model (lines) for different values of space time, at 375 °C (in molar fraction, Y_i). The kinetic model proposed for the main reaction allows quantifying product distribution at zero time on stream within a wide range of experimental conditions: temperature, in the range of 300-400 °C; space time, up to 0.2 $(g_{catalyst}\ h)(mol_C)^{-1}$; and different values of DME partial pressure.

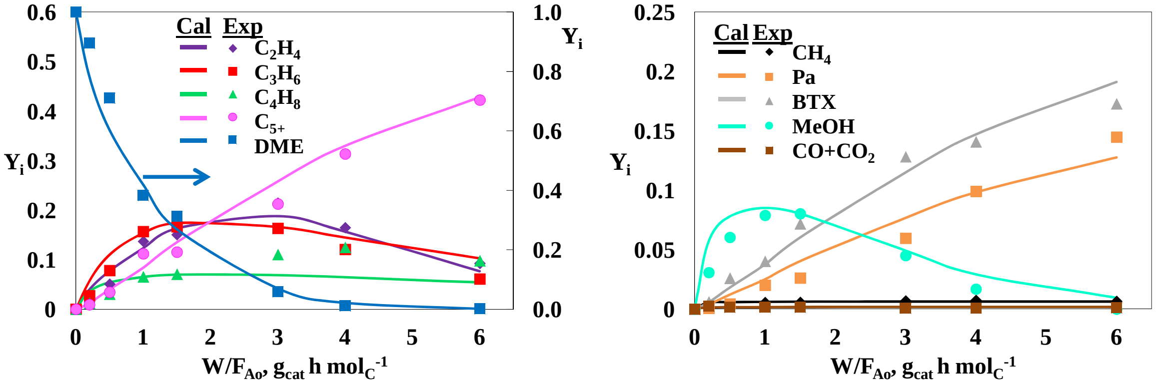

Figure 2. Comparison of experimental (points) and calculated (lines) values for the evolution of product with the space time (W/F_{Ao}). Molar fractions of major compounds (left) and minor compounds (right). Reaction conditions: raw DME, 375 °C

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PP-67

Ni-$Ca_{12}Al_{14}O_{33}$-CaO MULTIFUNCTIONAL CATALYST PREPARED BY ULTRASONIC ASSISTED METHOD FOR BIO-HYDROGEN FROM SORPTION ENHANCED BIOGAS STEAM REFORMING

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Hydrogen is an important gas whose demand significantly increases according to the advancement of fuel cell technology. Sorption enhanced steam reforming (SESR) is a promising process for hydrogen production. The advantages of SESR are: (i) reduction of overall size of the process as a reaction unit and a separation unit are combined in one unit operation; (ii) high methane conversion and hydrogen purity by the simultaneous reaction with CO_2 separation; (iii) lower capital and operating costs due to lower reaction temperature and cost of reactor materials. Development of efficient CO_2 sorbent is an important research topic. Generally, CaO shows high CO_2 sorption capacity (0.495 $g_{CO_2} / g_{sorbent}$) [1]. However, the main limitation of CaO is its low stability. To improve the stability of CaO, several researchers have investigated the addition of metal ions (Mg^{2+}, Sr^{2+} and Al^{3+}) into CaO structure [2, 3].

In this work, the Al modified CaO were synthesized by CaO hydration followed by wet mixing [3] with/without ultrasonic assistance denoted by UHW and HW, respectively. The sorbent stabilities are tested in a fixed bed quartz reactor and the results are shown in Figure 1(a). The modified sorbent (Al-CaO-UHW) shows stable CO_2 sorption capacity (approx. 0.28 $g_{CO_2} / g_{sorbent}$), while Al-CaO-HW shows a slight decrease of about 6.4 % over 10 cycles. Furthermore, the CO_2 sorption capacity of Al-CaO-UHW is higher than Al-CaO-HW. From the XPS results, it was found that more Al is found on the surface of Al-CaO-HW than Al-CaO-UHW. It is likely that the high concentration of inert $Ca_{12}Al_{14}O_{33}$ phase at the surface might suppress the carbonation reaction, which reduces the CO_2 sorption capacity.

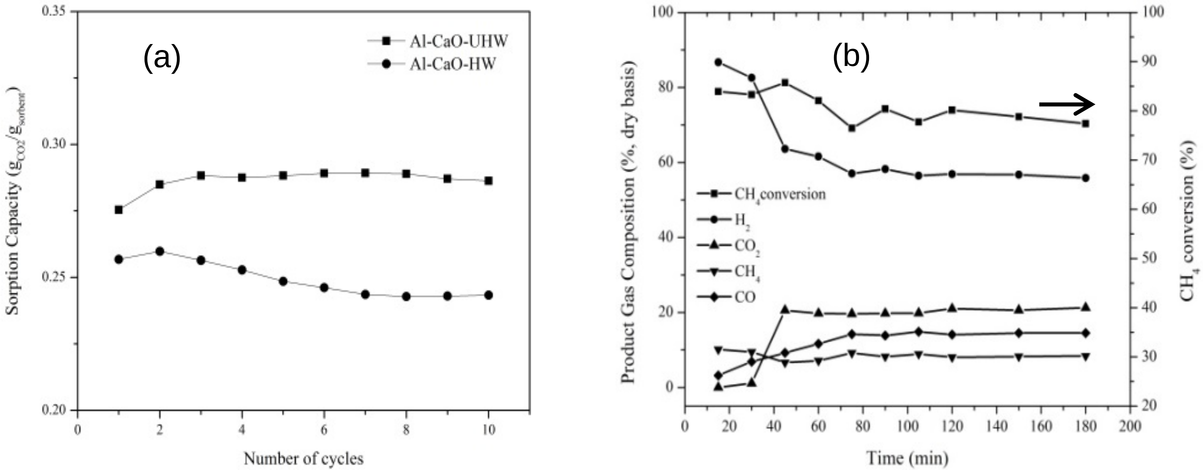

Figure 1. (a) Sorption performance of modified sorbents and
(b) Catalytic performance of Ni-Al-CaO-UHW

Table 1. X-ray photoelectron spectroscopy (XPS) analysis of modified sorbents

Sample	Atomic concentration at surface (%)		
	Al	Ca	O
Al-CaO-HW	8.7	9.7	81.6
Al-CaO-UHW	5.4	11.8	82.8

The catalytic activity of the multifunctional catalyst (Ni-Al-CaO-UHW) was tested for the sorption enhanced biogas steam reforming at a temperature of 600 °C, a pressure of 1 bar, S/C ratio of 3 and CH_4:CO_2 of 3:2. The results indicated that the highest H_2 purity and CH_4 conversion were approx. 87 % and 85 %, respectively at 15 min (Figure 1(b)). After that H_2 purity decreases while CO_2 increases because the sorbent could adsorb less CO_2. After 60 min, H_2 purity and CH_4 conversion are stable about 56 % and 78 %, respectively at post-breakthrough period.

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Acknowledgments

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CATALYTIC OXIDATION REACTIONS OVER Ce-Cu-OXIDE CATALYSTS

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It is widely accepted that the oxidation of VOCs over transition metal oxides, such as CuO-CeO_2 catalysts, occurs according to a Mars-van Krevelen type mechanism and proceed through lattice oxygen (nucleophilic attack) of the solid catalysts [1,2]. Therefore, the molecular oxygen is only required to reoxidize the reduced catalyst surface [3]. The interesting oxidation activity of Cu-Ce-O catalysts is created by the ability to reduce and re-oxidize of both CuO and CeO_2, which is enhanced by a strong interaction between these two phases (collective redox behavior). Indeed, CuO-CeO_2 is a more efficient catalyst for VOC total oxidation than the corresponding single metal oxides. This means that synergistic phenomena between CuO and CeO_2 may take place in oxidation processes. In this work, a set of CuO-CeO_2 catalysts with different Cu/Ce contents (denoted hereafter as Cu_xCe_{1-x} where x indicates the Cu/Cu+Ce atomic ratio) has been synthesized by the solution combustion synthesis (SCS) and their catalytic activity has been examined for the: i) total oxidation of ethene, Figure 1 (probe molecule for VOCs); ii) CO oxidation, Figure 2 iii) soot oxidation, figure not reported for brevity (probe reaction for Diesel soot combustion). As is known, CO oxidation can be a valuable reaction for probing the oxidation activity of ceria-based materials, whereas soot oxidation is a probe reaction for Diesel soot combustion (solid-solid-gas system). The prepared catalysts have been characterized by complementary techniques, including powder XRD, FE-SEM, N_2 physisorption at -196 °C, H_2-TPR, O_2-TPD and XPS to investigate the relationships between the structure and composition of materials and their performance toward oxidation processes. The Cu_xCe_{1-x} catalysts have specific surface areas and total pore volumes in the range of 3-31 m^2g^{-1} and 0.01-0.07 cm^3g^{-1}, respectively. The largest surface area and pore volume values are observed for the $Cu_{0.4}Ce_{0.6}$ catalyst, whereas further increase of Cu content leads to worse values of textural properties. As a whole, Cu_xCe_{1-x} catalysts exhibited higher oxidation activities compared to pure CuO and CeO_2 attributable to their easier reducibility and better redox properties, as revealed by H_2-TPR/O_2-TPD and XPS analyses.

However, the beneficial effect of the SSA on the overall oxidation activity may be also possible. These findings suggest that Ce-Cu mixed oxides cooperate synergistically to lead higher oxidation activities via collective properties on the catalyst surface, such as electrical conductivity, surface or bulk oxygen anion mobility. On the other hand, the activity for soot oxidation under tight soot-catalyst contact condition increased a function of the Ce-content as well as the structural properties play a key role for this solid-solid-gas phase reaction [4]. Thus, the best catalytic performances have been obtained with pure ceria.

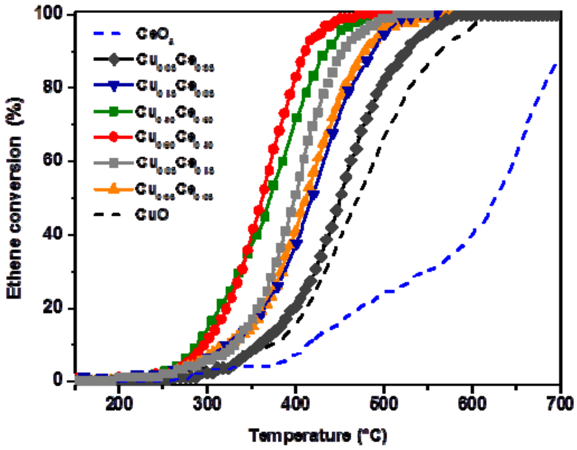

Figure 1. Conversion of ethylene to CO_2 as a function of temperature

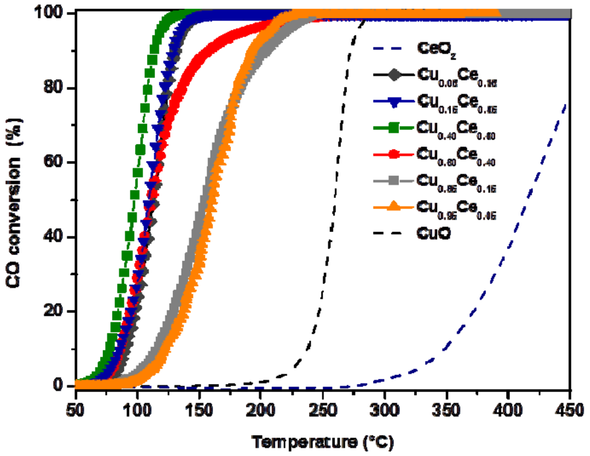

Figure 2. Conversion of CO to CO_2 as a function of temperature

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COOPERATIVE PHENOMENA IN OXIDATION CATALYSIS: CO OXIDATION OVER MIXED OXIDE CATALYSTS

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During the last few decades, Ceria-based materials have received much attention in applied catalysis, thanks to their notable redox properties and OSC that allow quick intake and release of oxygen. Moreover, it has been observed that inserting aliovalent cations, like Zr^{4+} and Pr^{3+}/Pr^{4+} into Ceria framework gives more surface oxygen vacancies (structural defects) as well as redox active sites [1-3]. As is known, nanostructured Ceria-based catalysts are of particular interest for oxidation catalysis and then several approaches have been exploited to synthesize small Ceria nanoparticles, including hydrothermal/solvothermal, sol-gel, microemulsion and precipitation. In the present work, sets of Ceria, Ce-Zr (Ce 80 at. %, Zr 20 at. %), Ce-Pr (Ce 80 at. %, Pr 20 at. %) and Ce-Zr-Pr mixed oxide catalysts (Ce 80 at. %, Zr 10 at. % and Pr 10 at. %) have been prepared by the solution combustion synthesis (SCS), the multi-inlet vortex reactor (MIVR) and the hydrothermal synthesis.

Their catalytic activity has been tested for CO oxidation, a prototypical reaction for probing the oxidation activity of Ceria-based materials [4]. The catalysts have been characterized by complementary techniques, including powder XRD, FE-SEM, N_2 physisorption at -196 °C, H_2-TPR, O_2-TPD and XPS to investigate the relationships between the structure and composition of materials and their performance.

As shown in Figure 1, better results for CO oxidation have been obtained with mixed oxides prepared by SCS method (performance scale: Ce-Zr-Pr > Ce-Zr > Ce-Pr) rather than pure Ceria, thus confirming the beneficial role of multicomponent catalysts for this prototypical reaction. Since CO oxidation occurs via a Mars-van Krevelen (MvK) type mechanism over Ceria-based catalysts, it appears that the presence of both Zr and Pr species into the Ceria framework improves the oxidation activity, via collective properties, such as electrical conductivity, surface or bulk oxygen anion mobility. The Ce-Zr-Pr catalyst, indeed, exhibited easier reducibility and better redox properties, as revealed by H_2-TPR, O_2-TPD and XPS analysis. In order to evaluate the possible role of the particle sizes on the catalytic activity, the multi-inlet vortex reactor (MIVR) has been used for application in flash nanoprecipitation. As expected, better results for CO oxidation have been obtained with mixed oxides than pure Ceria, thus confirming the role of collective properties for this oxidation reaction. In order to better evaluate the structural properties of the nanoparticles for this reaction, a set of nanostructured Ceria-based catalysts, with well-defined crystalline planes, obtained via hydrothermal procedure (namely Ceria, Ce-Zr, Ce-Pr, Ce-Zr-Pr, Figure 2) has been tested. Surprisingly, the activity for CO oxidation followed the order of reactivity: Ceria > Ce-Zr > Ce-Pr > Ce-Zr-Pr. This trend is opposite with respect to that obtained for catalysts synthesized by either SCS or MIVR. This finding further confirms that collective properties of metal oxide catalysts (namely surface reducibility and redox properties) depend on both electronic and geometric factors.

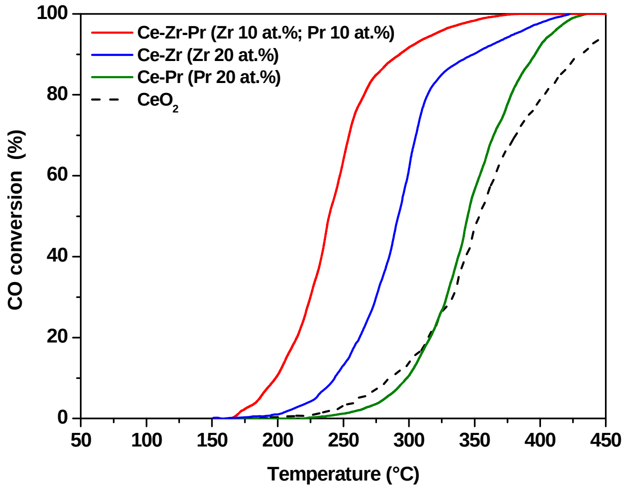

Figure 1. Conversion (%) of CO to CO_2 as a function of the temperature

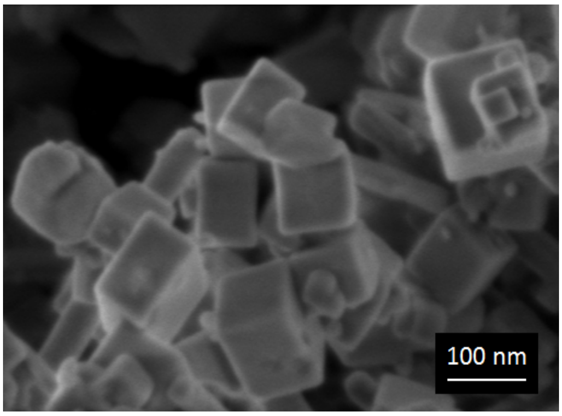

Figure 2. FESEM image of the Ce-Zr-Pr catalyst obtained by hydrothermal synthesis

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CONVERSION OF HYDROCARBONS TO SYNGAS IN A NON-PREMIXED REVERSED-FLOW POROUS BED REACTOR

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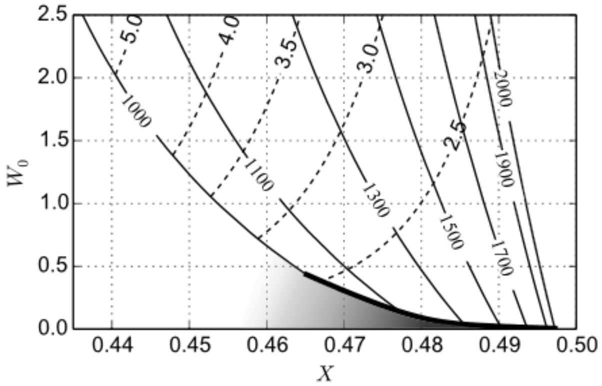
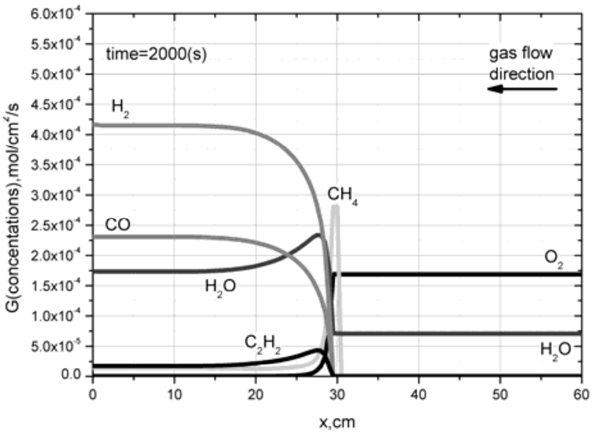
The non-catalytic partial oxidation in superadiabatic regimes in a porous matrix provides an attractive means for hydrocarbons reforming into syngas. Those processes rely on high reaction temperature, while providing a heat recuperation via the gas–solid heat exchange. Thus, a high reaction temperature might be combined with a low energy expenditure [1]. A superadiabatic partial oxidation reforming process can be achieved in a reverse-flow reactor filled with an inert refractory porous material. The porous bed accumulates heat as the hot gas flows through it. When the bed heats to the outlet, the flow direction is reversed and the heat of the bed is used to preheat the incoming gas. The studies of filtration combustion of ultra-rich methane–oxygen–steam mixtures in porous matrices show that the process "chooses" the temperature too low to achieve reactions of water with methane [2, 3].

A new approach to partial oxidation in a reverse flow reactor has been proposed in [4]. The reversed flow reactor in established cyclic process operates as follows. During the first half-cycle, methane–steam mixture is supplied to the reactor at one end. The mixture filters through the porous matrix heated during previous cycle, heats up and reaches the middle part of the reactor at a high temperature. Oxygen is supplied to the center of the reactor and reacts with methane at high temperature. The hot syngas from the reaction zone filters through the porous bed and lends its sensible heat to the porous matrix in the second part of the reactor. The syngas leaves the reactor being substantially cool. When the porous bed in the second part heats up, the direction of the gas flow is switched to reverse and operation of the reactor during the second half-cycle proceeds mirrorwise. We provide a simplified model to outline the basic dependences of the process on control parameters, namely, flowrates of methane, steam, and oxygen [5]. The calculation is based on the assumption that composition of syngas is that equilibrium at the combustion temperature. The conservation equations for carbon, oxygen, and hydrogen and conservation of energy in the reaction zone (in the absence of heat loss) are supplemented with the equation of thermodynamic equilibrium. Fig. 1 shows the combustion temperature (solid lines) and H_2/CO ratio (dotted lines) in syngas as dependent on O_2/CH_4 molar ratio X and O_2/CH_4 ratio W_0 in the reactants supplied.



This approach provides a high energy efficiency of conversion and can also be applied to air-steam conversion of hydro-carbons, in which case air-steam mixture should be supplied at the reactor end and hydrocarbons supplied to the hot reaction zone in the center.

On the way to practical implementation of this process one must both theoretically and experimentally investigate such aspects as finite rates of the kinetics of the reactions, the heat loss, structure of the reaction and reactant mixing zones, transients associated with ignition and flow reverse, etc. The computational model describing kinetics of methane conversion taking into account heterophase reactions of carbon deposition [3] was used to study the process in the non-premixed reactor.



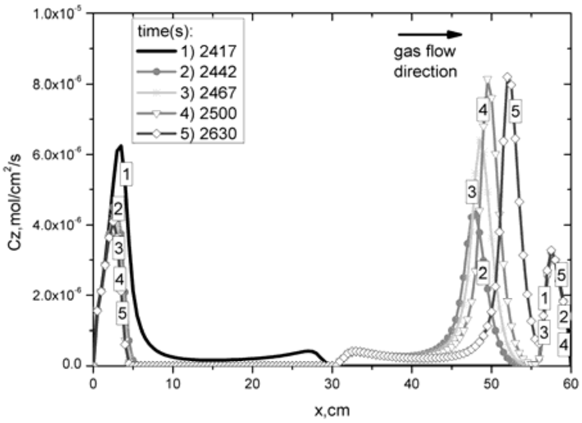


Fig. 2 shows spatial distributions of flows at a certain instant and Fig. 3 distribution of surface concentration of soot during two cycles of air-steam conversion of methane at $x = 0.6$; $w_0 = 0.25$.

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MODIFICATION OF GLASS FIBER CATALYST SURFACE BY ADDITIONAL LAYERS OF SILICA AND CARBON NANOFIBERS

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There are various methods of producing carbon nanofibers (CNF). The most common method is the catalytic decomposition of light hydrocarbons on the catalyst [1]. The catalyst normally used metal supported on a porous carrier [2]. In this paper, we demonstrated the possibility of the use of glass fiber supported nickel catalyst in the process of catalytic decomposition of light hydrocarbons.

The samples of Ni-containing glass-fiber catalysts (GFC) were prepared by means of surface thermo-synthesis IST method [3]. The preparation included the supporting of the thin layer of porous SiO_2 at the external surface of glass micro-fibers; impregnation of this layer with water solution of the active component precursor (nickel acetate) and fuel additive (glycine), followed by drying and thermal treatment. The prepared GFC sample contained NiO in amount of ~2.0 % (calculated for metal Ni), the specific surface was equal to 34 m^2/g, pore volume 0.03 cm^3/g, average pore diameter ~8 nm.

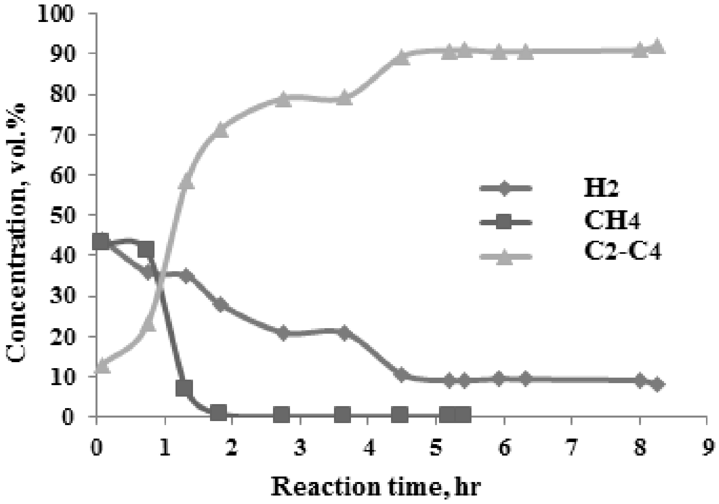

Fig. 1. Change of volume concentrations of LPG pyrolysis products at Ni/GFC in time

The sample carbonization was carried out in the flow installation Autoclave Engineers BTRS-Jn in a metal tubular reactor at a temperature of 450°C. Mixture of propane and butane (LPG) was used as a carbon source. During the first hour, LPG conversion approached 90 %. Significant concentrations of methane (up to 50 vol %) and hydrogen (up to 40 vol %) were observed at reactor outlet (Fig. 1). Methane concentration dropped to 0 after 1.5 hours, the hydrogen concentration continued to steadily fall further 6 hours.

The nano-fibrous carbon growth at the Ni/GFC was equal to 1.02 grams. It corresponds to 131 % of the initial GFC mass, carbon yield is 65 g per g of nickel. The formed layer of carbon is strongly attached to the glass fiber support and the whole system is mechanically stable. Surface area of the carbonized GFC was equal to 100 m^2/g, a total pore volume – 0.18 cm^3/g. The synthesized sample is strongly hydrophobic.

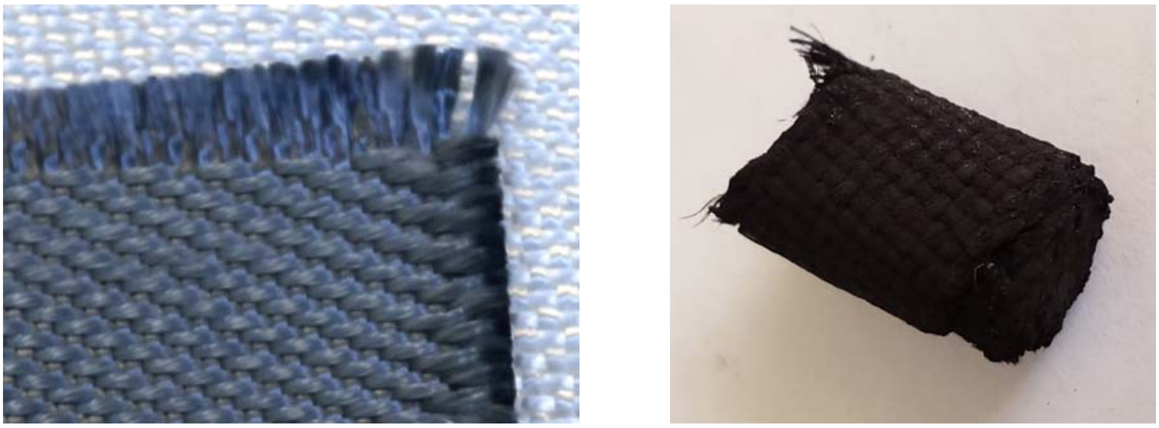

Fig. 2. View of the initial (left) and carbonized (right) Ni-based glass fiber catalyst

As shown by theoretical estimation [4], the GFC's structured cartridges are characterized with the very high specific mass transfer efficiency and low pressure drop, thus providing the great engineering potential of structured fiber-glass catalytic systems. The synthesized material with nano-fibrous carbon layer may be used in practical purposes as the fibrous catalyst, adsorbent or support for fibrous catalysts, thus significantly widening the range of potential practical application of GFCs.

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PP-72

A MODEL FOR CATALYTIC SYNTHESIS OF MWCNT IN A FLUIDIZED-BED REACTOR: EFFECT OF REACTION HEAT ON THE GROWTH OF LATERAL CARBON DEPOSITS

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Previously, the mathematical model describing synthesis of multilayer carbon nanotubes (MWCNT) via catalytic CVD technique in a fluidized bed (FB) reactor was developed [1]. The model considers significant increase fluidized bed in volume during the synthesis. It allows optimizing the regimes of periodic discharge of product from the reactor and reload of new catalyst portions in it. In the present work, this model have been extended to describe the growth of lateral carbon depositions (LCD) on external walls of nanotubes and variation of the bed temperature due to reaction heat and catalyst deactivation. LCD formation on MWCNT's surface significantly affects their bulk density of nanotubes, specific surface area, surface defectiveness, electrical conductivity. Thus, one should control the fraction of LCD in the product.

Appreciable variation of the bed temperature (about 25 °C) during each cycle of MCWNT growth in FB from ethylene as a precursor have been experimentally observed. This can be accounted for exothermic nature of ethylene decomposition. Temperature deviation may have significant impact on the fraction of LCD as well as on the diameter distribution of MWCNTs.

In the developed model, we presume heat transfer between fluidized bed and heater walls to be fast in comparison with the time of reaction cycle, Therefore, the reactor temperature can be found from steady-state energy balance. The reaction heat for carbon nanotubes formation from ethylene for the considered temperatures is taken $Q_r = 1.59 \cdot 10^6$ J/kg MWCNT. The other details of the developed model are similar to the model formulated in [1].

To describe the kinetics of LCD growth we used the experimental data obtained in Boreskov Institute of Catalysis for the temperature range of 820-1000 K and C_2H_4 volume concentrations in the C_2H_4/Ar mixture from 0.135 to 0.670. The rate of LCD formation can be expressed in the form $dm_{lt}/dt = M_C m_{nt} k_0 \exp(-E/RT) X_1^2 P_r^2 S_{nt}$, where m_{nt} is the mass of nanotubes, E= 257 кДж/моль, k_0 =3.32·10^5 mol/(m^2·s), X_1 is the relative volume concentrations of gas-precursor, P_r is the pressure in the reactor, S_{nt} is the specific surface area of MWCNT, M_C is the carbon molar mass.

Typical calculated oscillations of the bed temperature during two cycles of MWCNT synthesis are shown in Fig. 1. The presented results relate to the base temperature of reactor heater T_f =950 K.

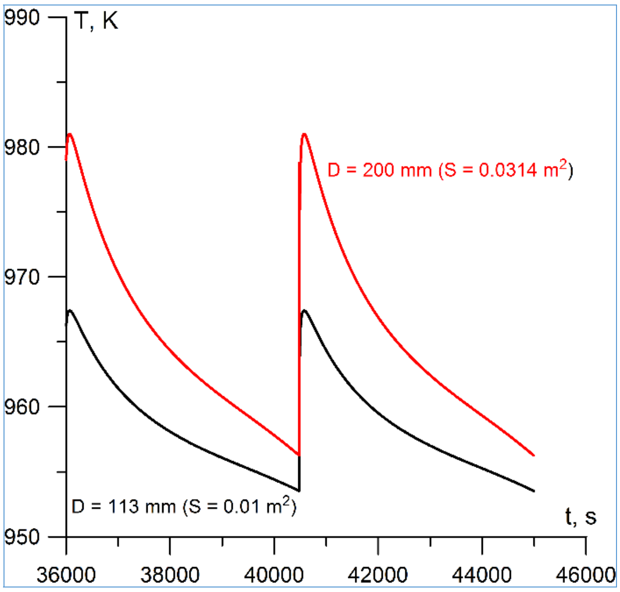

Figure 1. Calculated temperature oscillations during MWCNT synthesis in fluidized bed

The temperature of the reactor increase with its size. This is due to the linear increase of the ratio “evolved heat to heat losses through the reactor walls” with the reactor diameter D. Maximum temperature is attained in the beginning of the cycle, just after loading the fresh catalyst. The amplitudes of temperature jump are rather high (up to 30 K) which affect the mass fraction of carbon lateral depositions (Table 1). It should be noted that the reaction heat depends on the type of gas-precursor. For example, in the case of propane-butane mixture, negative heat of their decomposition should lead to decreasing bed temperature.

Table 1. Effect of temperature oscillations on the LCD fraction in the product for the different reactor diameters

Reactor diameter D, m	LCD mass fraction	
	Q_r = 0	Q_r = 1.59·10^6 J/kg
0.113	0.013	0.017
0.200	0.013	0.021

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KINETIC CHARACTERIZATION OF ZEOLITIC MTO/MTH CATALYSTS WITH ADVANCED TEMPORAL ANALYSIS OF PRODUCTS (TAP-3) INSTRUMENT

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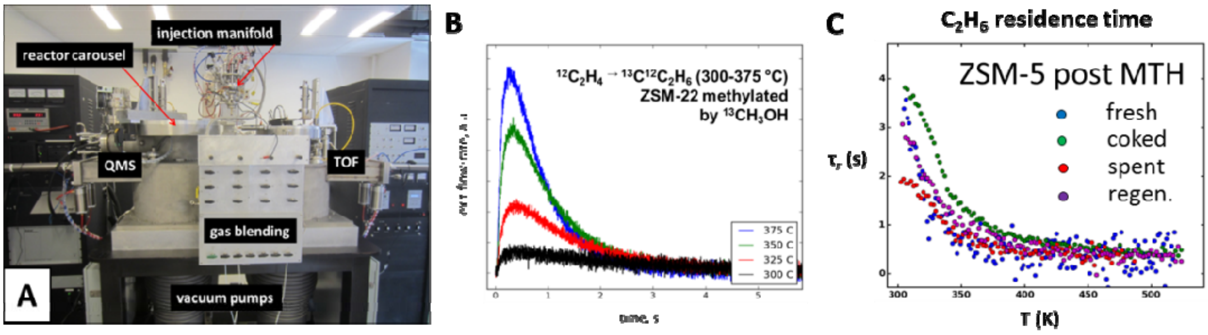
Methanol-To-Hydrocarbons (MTH) and Methanol-To-Olefins (MTO) processes catalyzed by zeolitic materials could become the key steps in large-scale valorization of alternative carbon sources and natural gas to fuels and chemicals [1]. Truly fundamental insights into their catalytic properties are urgently needed in order to further improve the performance of zeotypes through rational manipulation of their structure. However, in-depth kinetic characterization of zeolite-driven chemistry presents a formidable challenge due to the inherent complexity of reaction mechanisms and the strong coupling between chemical reactions, confinement effects, and diffusion phenomena in zeolitic frameworks.

Herein, an advanced 3rd-generation TAP instrument was used to characterize ZSM-22 and ZSM-5 zeolites in two MTO/MTH-related case studies. Time-resolved (1 ms) TAP pulse-response experiments are uniquely suited for detailed kinetic characterization of coupled reaction/diffusion processes [2] because they enable precise control over the catalyst state (e.g. oxidation degree, surface coverage, and pore occupancy) and facilitate the deconvolution of different reaction steps and transport processes within the material. In addition to the standard TAP setup based on high-speed (100 μs) gas injectors (1 nmol/pulse) and a Quadrupole Mass Spectrometer (QMS), the TAP-3 instrument used in the present study (Figure A) also features *in vacuo* sample carousel for high-throughput data collection as well as a Time-Of-Flight (TOF) mass-spectrometer for increased mass-resolution and simultaneous monitoring of multiple m/z ratios.

The first case study elucidated the intrinsic kinetics of the reaction between methyl groups bonded to Brønsted acid sites of ZSM-22 zeolite and the incoming C_2-C_4 olefin molecules at 300-400 °C [3]. The aromatics cycle of the "dual cycle" MTO/MTH mechanism is hindered in ZSM-22 due to the spatial constraints of its 1D

TON topology, which allowed measurements of single-step methylation kinetics in isolation from the rest of the mechanism. The resulting kinetic parameters could be compared to the DFT-derived values, and provided valuable insights into the confinement effects in zeolites.



In the second case study, molecular traffic of C_2H_6 and C_2H_4 probe molecules in and out of nanoporous confines of ZSM-5 zeolite at 50-200 °C was investigated at different stages of catalyst's life-on-stream during MTH process. Residence times of probe molecules inside fresh, partially-coked, fully spent, and *in situ* regenerated samples suggest that the double bond of C_2H_4 facilitates the entry of this guest molecule into the host framework, as compared to the single bond of C_2H_6. Moreover, pronounced differences in intra-framework behavior of both guest molecules were observed between different samples (Figure B). These results are discussed in light of the current understanding of ZSM-5 deactivation and are used to establish TAP as a sensitive tool for discriminating microporous materials based on their interactions with common guest molecules.

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"EMISSIONS TO LIQUID FUELS" VIA METHANE DRY REFORMING

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The growing trend of CO_2 emissions driven by the increase of global energy consumption makes mandatory a commitment of the scientific community to investigate routes for CO_2 valorisation. Chemical recycling may significantly contribute to a reduction of its emissions and represents an interesting alternative to the on-going projects on carbon capture and storage (CCS). Among the different alternatives for chemical recycling, methane dry reforming, DRM ($CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$) is an efficient route to convert CO_2 into syngas [1], which can be used to produce liquid fuels and platform chemicals via Fischer-Tropsch (FT) synthesis as shown in Figure 1.

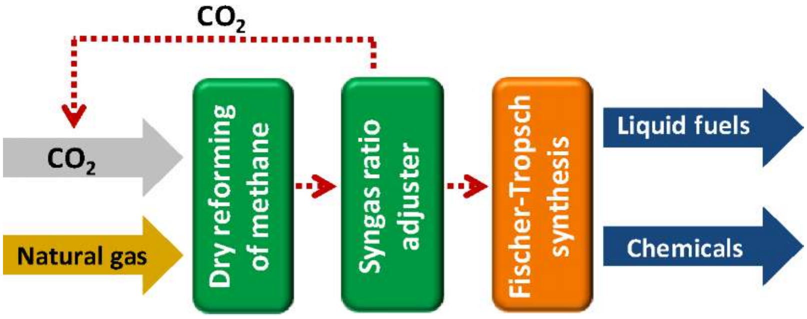

Figure 1. CO_2 conversion to chemicals and fuel via DRM and FT

In addition, this process possesses potential thermochemical heat-pipe applications for the recovery, storage and transmission of solar and other renewable energy sources by using the large heat of reaction and the reversibility of this process. However, the main drawback of this process is the rapid deactivation of the catalysts mainly due to carbon deposition and sintering of the metallic phase. In order to overcome this stability issue, this work aims to develop a novel family of advanced heterogeneous catalysts with enhanced long-term stability and high selectivity towards syngas. Furthermore, a careful desing of the dry reforming reactor is also proposed targeting the most efficient DRM-FT coupling.

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EFFECT OF THE MASS RATIO OF METALLIC AND ACID FUNCTION ON A BIFUNCTIONAL CATALYST IN THE DIRECT SYNTHESIS OF DME FROM SYNGAS AND CO_2

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Dimethyl ether (DME) can be regarded as an alternative of the fosil fuel [1] due to it can be synthesized from syngas obtained from alternative sources (natural gas, coal, biomass o waste) [2]. The synthesis of DME in a single stage, or Syngas to DME process (STD), integrates methanol synthesis and its dehydratation on a bifunctional catalyst (metallic function for the methanol synthesis and acid function for the dehydration). The advantage of the single stage synthesis is that the thermodynamic limitations are reduced allowing raising the operation temperature and using CO_2 as feedstock.

The aim of this work is to study the influence of the mass ratio, between the metallic and the acid function, in the direct synthesis of DME determining CO_x conversion, and DME yield and selectivity.

The catalyst was prepared employing $CuO\text{-}ZnO\text{-}ZrO_2$ as metallic function, that provides a high activity in mixtures with CO_2, and SAPO-11 as acid function, because of its moderate strength and high hydrothermal stability by physical mixture.

The runs were carried out in a fixed bed reactor at 275 °C, 30 bar, a space time of $5\ g_{cat}\ h\ mol_C^{-1}$, time on stream up to 2 h, feeding syngas and CO_2 ($H_2/CO_x = 3$, $CO_2/CO = 1$), and the reaction products have been analyzed continuously in a Varian CP-4900 micro-gas chromatograph.

Figure 1 shows the yield of DME, methanol and paraffins obtained using a bifunctional catalyst with different mass ratio of metallic and acid function (M/A). It is observed that the highest conversion of CO_x and DME yield, with low paraffin yield, is reached with the 1/3 ratio. Furthermore, the DME yield increases from 1.7 to 7.9 % (from 2/1 to 1/3) and with higher M/A ratios DME yield decreases, as do the CO_x conversion.

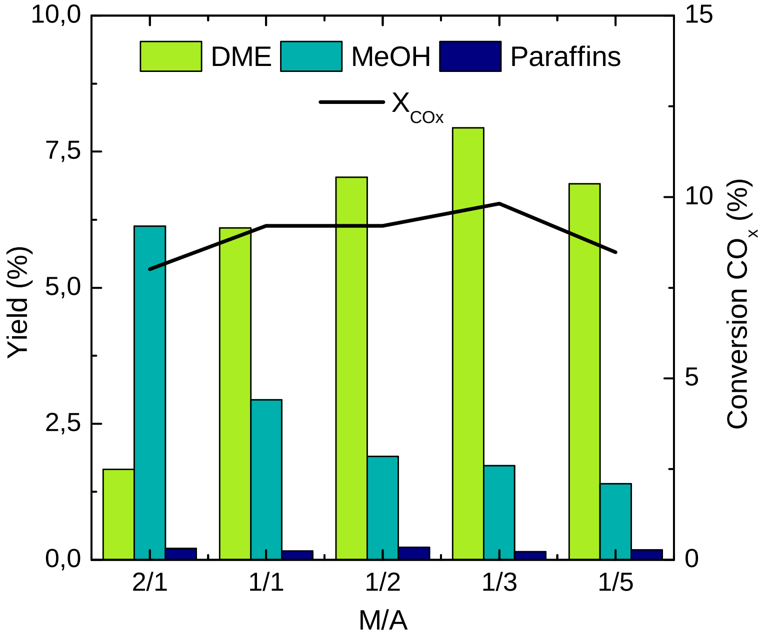

Figure 1. Effect of the mass ratio in COx conversion and yields of DME, methanol and paraffins

These results state that CuO-ZnO-ZrO_2/SAPO-11 bifunctional catalyst is suitable for being used in the STD process co-feeding CO_2 and syngas, being 1/3 the optimum M/A ratio for this process becouse of its high DME yild and low paraffins production.

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Acknowledgements

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PP-76

BUBBLE COLUMN REACTOR FLUID DYNAMIC EVALUATION AT PILOT PLANT SCALE FOR RESIDUE AND EXTRA-HEAVY CRUDE OIL UPGRADING TECHNOLOGY

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Bubble column reactors are multiphase contacting devices used in a wide variety of industrial application, due to their easy construction, operation, high heat transfer rate and overall mass transfer coefficient. Venezuelan Oil Company Research Center has been developing technologies to convert extra-heavy crude oil that use this type of reactors. Volumetric gas hold up, flow pattern, average gas bubble size, average interfacial area, residence time distribution (RTD), dispersion coefficient, Péclet number are important design parameters for bubble column reactor and for a proper scale up of them. Several cold model experiments have been proposed to determine the previously mentioned parameters at atmospheric conditions, using a plexiglas bubble column reactor at pilot plant scale unit (12 cm diameter), see Figure 1. It was also evaluated our own design of internal trays (plates) in the reactor. Air-tap water and air-light oil systems have been used. The oil has similar physical and chemical properties to the feedstock (vacuum residue) on operating conditions. A wide operating condition range was applied, superficial gas velocity between 0.5-10 cm/s, liquid flowrate between 15-65 l/h. General speaking, working without internal trays was found that gas hold up increase along the reactor and it was possible to identify heterogeneous bubble, transition and turbulent flow pattern areas at different superficial gas velocities for the air-light oil system [1]. It was also determine that average gas bubble size increase along the reactor at bubble regime from 2-5 mm but at turbulent regime, stay oscillating between 1-3 mm. The average bubble diameter of the air-tap water system is always higher (at least 4 times) than the air-light oil system [2,3,4]. At the same reactor height, average gas bubble size decreases with the superficial gas velocity. [5] Average interfacial area increases exponentially with superficial gas velocity at any reactor height, till 1412 m^2/m^3 for the air-light oil system but, at bubble flow regime, the average interfacial area is lower than 100 $m^2/m^{3,}$ which negatively impact the reactor performance. Internal trays in the reactor always increase gas hold up at any condition or system used [4,6].

Residence time distributions curves, Péclet numbers and dispersion coefficients founded, show that this reactor with this kind of design internal trays still tends to be a complete mixing reactor under the operating conditions used. The new RTD curve was displaced on time because the death space created by the internal inside the column [7,8].

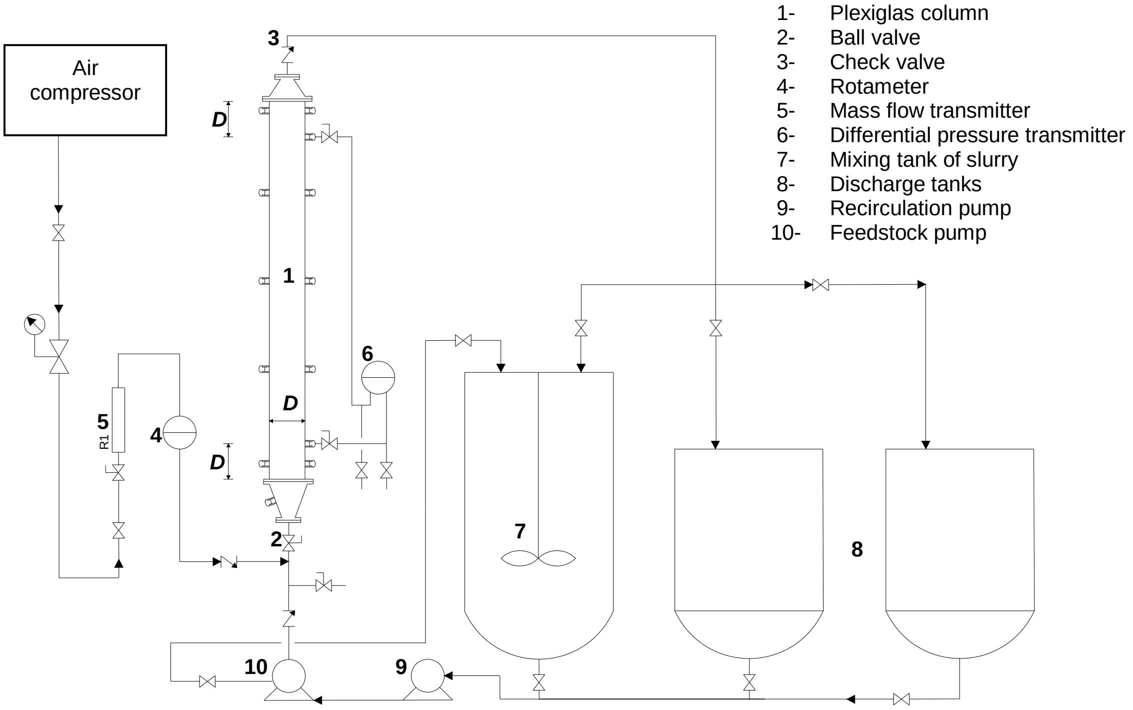

Figure 1. Schematic diagram of the experimental apparatus

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KINETIC MODEL OF OXIDATIVE CONVERSION OF METANE TO SYNGAS

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At the moment, there are three methods suitable for industrial production of synthesis gas from methane:

steam conversion:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H = +206\ kJ/mol \qquad (1)$$

oxidative conversion:

$$CH_4 + ½\,O_2 \leftrightarrow CO + 2H_2 \qquad \Delta H = -\,35{,}6\ kJ/mol \qquad (2)$$

carbon dioxide conversion:

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad \Delta H = +\,247\ kJ/mol \qquad (3)$$

The main industrial method of methane conversion to syngas is hitherto steam reforming (1). Due to the high endothermicity of the process its main drawbacks are the need for supplying large quantities of heat and transfer it to the catalytic layer. From this viewpoint, more attractive is weakly exothermic reaction (2). The wide applying of the reaction (2) for commercial production of synthesis gas hampered by a lack of stable, active and selective catalyst for this reaction, and the absence of reliable fixed scheme and sequence of the reactions represented as a total formal equation (2). To establish the scheme of the reactions and to obtain their kinetic description, we used the results of experiments carried out on the catalyst $NdCaCoO_4$, developed at the Gubkin Russian State University of Oil and Gas, which meets all the requirements listed above.

Kinetic experiments were performed in a continuous tubular reactor with an equivalent diameter of 4 mm and a height of catalyst layer not more than 0.5 cm. Despite the temperature of the reactor was regulated it was strongly dependent on the feed rate of the initial mixture due to the high thermal effects of the reactions. For this reason, it was impossible to fix both the total flow rate and temperature of the feed mixture in a catalyst layer. As a result for the choice of the reaction scheme and development of the kinetic model we had the results of 68 experiments in which the temperature values and the total feed of the initial mixture both were spontaneously fixed in the range of 860-985 °C and 1588-6156 ml of gas mixture per gram of the catalyst per hour. The other data for analysis of the scheme and kinetic model were the compositions of feed mixture which were strongly fixed and the content of CO, CO_2, CH_4, O_2 and H_2 in the output of the reactor determined by GLC in each experiment. The water formed was calculated form the material balance.

The yields of water, hydrogen, CO and CO_2 obtained in all 68 experiments give almost uniform dependency from methane conversion wherein the formation of hydrogen and CO begins only after complete consumption of oxygen (75 % of not converted methane) (Fig. 1). This indicates that in the first stage the only reaction of methane combustion occurs:

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2H_2O \qquad (4)$$

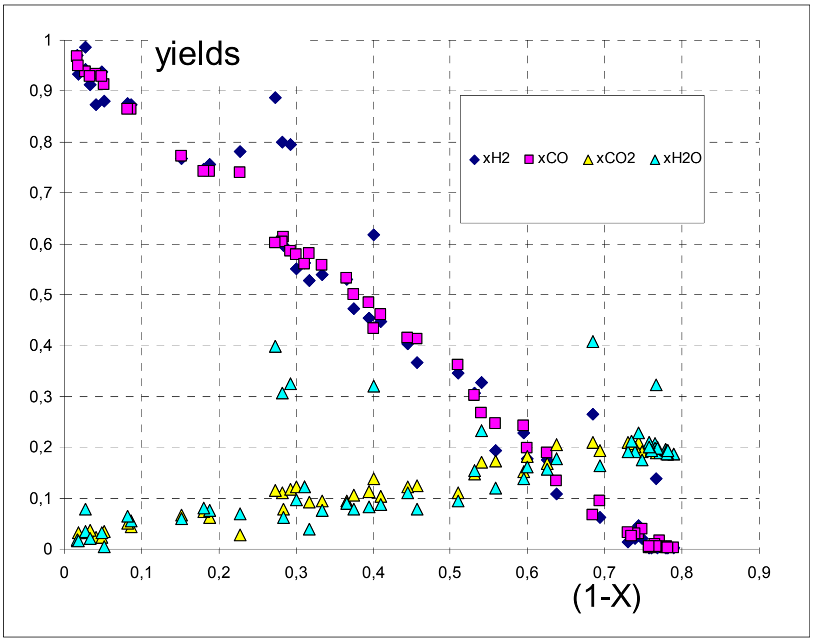

Fig. 1. The dependence of the yields of H_2, CO, CO_2 and water from the portion of not converted methane (1-X). (X – methane conversion)

And only after complete consumption of oxygen synthesis gas begins to form on the reactions of steam (1) and carbon dioxide (3) conversion. Equality of the yield of CO and hydrogen, as well as water and CO_2 obtained at different methane conversions shows equal rates of the reactions (1) and (3) in all the temperature range 860-985 °C.

Based on the finding that a total formal equation of oxidative conversion (2) really reflects a sequence of reactions (4), (1) and (3) developed kinetic model adequately describes all 68 experiments conducted.

Acknowledgment

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PP-78

TECHNOLOGICAL APROACH FOR PRODUCTION OF BULK ORGANICS FROM RENEWABLE SOURCE

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Intensive development of biotechnological synthesis of organic acids makes possible to produce bulk organic substances on their base. One of the most perspective is lactic acid (LA). Conventionally LA is being produced by batch fermentation as a ammonium salt (pH of fermentation medium ca. 6–7), and is separated throw calcium salt formation, that cause large amount of waste of calcium sulphate (1 ton per 1 ton of LA). Now the new strains and fungi are developed which produce LA in a free form (pH of fermentation medium ca. 3,5), but selectivity of LA formation is not more than 70 %. Moreover the batch fermentation possesses low specific productivity about 5 g(LA)/(L×h).

In present work we investigated new technological approach for synthesis of Butyl Lactate (BL) from LA from renewable source throw LA fermentation. BL as such is effective green solvent and a semi product for synthesis of bulk organics such as propylene glycol, highly pure lactic acid, lactate esters, lactide, polylactide (PLA), acrylic acid and its derivatives (Figure 1). This approach allows increasing of specific productivity of fermentation and avoid of gypsum.

Fermentation of LA is carried out in a membrane bio-reactor in a continuous mode at pH = 6-7 (pH is maintained by NH_3 neutralization), the product (fermentation solution) is periodically output throw ultra-filtration membrane, while sells remain inside reactor and acts as suspended heterogeneous catalyst. Under in optimal conditions using *Lactobacillus paracasei* membrane bio-reactor was working during 874 h with following parameters: LA yield not less then 95 %, final concentration of LA up to 120 g/L, specific productivity 45-70 g(LA)/(L×h).

In order to use fermentation solution for BL synthesis it is necessary to purify it from high-molecular impurities (products of cells' lysis). We used method of nano-membrane filtration. The influence of various conditions (pressure, temperature, flow rate, rate of withdrawing) on purification rate was investigated. The following parameters of purification were achieved: yield of purified ammonium lactate more then 85 % and rate of purification from high-molecular impurities up to 90 %.

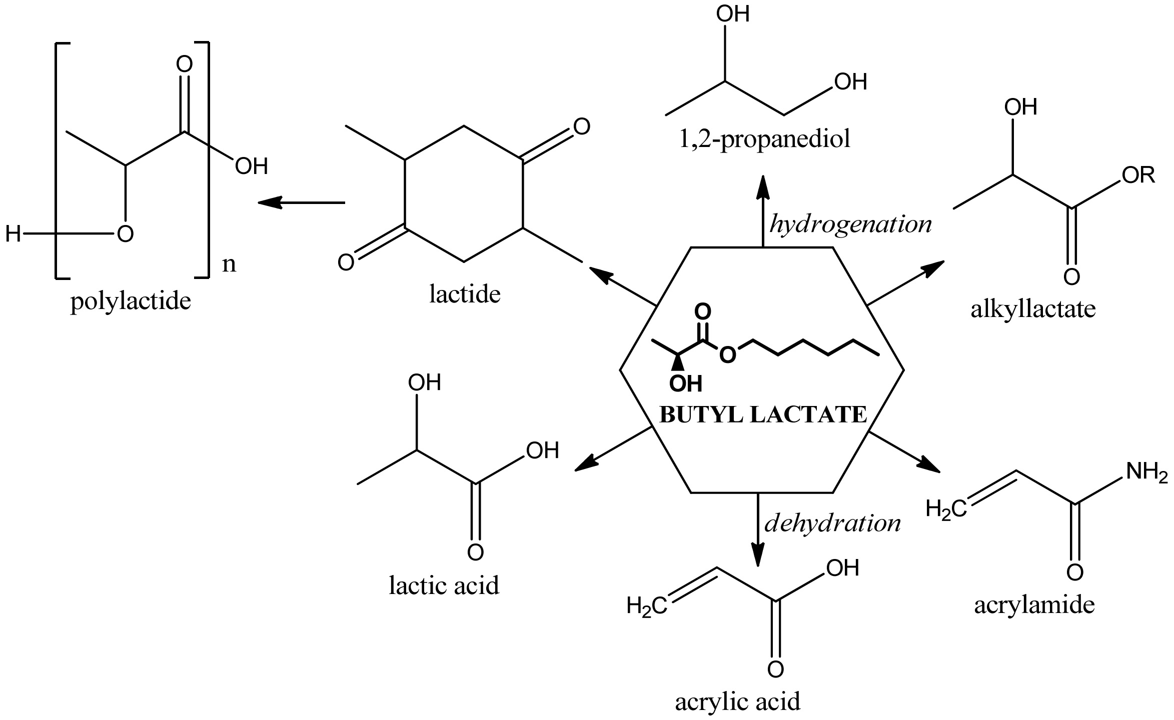

Figure 1. Butyl Lactate as a platform for synthesis of bulk organics

The synthesis of BL was investigated in two types of reactor: (1) semi-batch reaction-rectification reactor, and (2) continuous column reactor. It was established that semi-batch reactor allows achieving of highest yield of BL up to 95 % using purified fermentation solution (whereas using of native fermentation solution gives yield in a range 65-80 %). The continuous column reactor allows obtaining higher productivity then semi-batch one but yield of BL is lower – not more then 60 %.

The data obtained are the basis for optimization of technology of effective route for production of bulk organics from renewable source.

Acknowledgements

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PP-79

EXPERIMENTAL AND MODELING STUDY OF SOLID STATE NH_3BH_3-BASED MATERIALS AS A PROMISING WAY OF HYDROGEN STORAGE FOR SMART REACTORS

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In the long-term strategy to develop environmentally friendly hydrogen-based power technologies and to widen the scope of their practical applications, the task of finding safe and efficient ways for hydrogen storage is among the most important ones. The study of solid hydrides ($NaBH_4$, $LiBH_4$, MgH_2, NH_3BH_3, etc.) as potential sources of hydrogen and the development of optimal ways to release it is a rapidly developing field of research. In hydrogen storage capacity, these compounds have no rivals. Among them, ammonia borane (NH_3BH_3, AB) is of particular interest because of its very high content of hydrogen (19.6 wt%) and its high stability in air at ambient temperatures. In the solid-state dehydrogenation (thermolysis) of AB the release of 2 molecules (equivalents) of H_2 takes place stepwise to produce polymeric products: $(NH_2BH_2)_x$ at ~ 100 °C, $(NHBH)_x$ at ~ 150 °C. The release of the third molecule of hydrogen to form BN occurs at a higher temperature (>500 °C). Practical application of AB and the development of smart AB-based reactors requires solution of some problems, among which lowering hydrogen release temperature and increasing the rate of hydrogen generation are important ones [1].

This work is a systematization of the results on the low-temperature destabilization of AB in contact with different modifiers (including catalysts). It also proposes a mathematical model of hydrogen generation which takes into account heat and mass transfer processes in the solid-state reaction layer in an externally heated tubular reactor.

The efficiency of the low-temperature H_2 generation from a solid-state «AB-modifier» material is determined by a number of factors such as the modifier properties, including its heat conductivity, the extent of hydride/modifier contact and the presence of water. On the basis of the obtained results an approach has been suggested to explain the high rate of hydrogen evolution at temperatures <100 °C, where destabilization of dihydrogen $BH^{\delta-}$-$^{+\delta}HN$ bonds in the NH_3BH_3 structure is discussed.

The role of the composition, properties and geometry of the «AB-modifier» reaction layer has been established. It was found that in the tubular reactor the geometry of the hydride-containing reaction layer is a key factor in determining the rate of AB decomposition. This demonstrates the necessity of considering heat and mass transfer. Thus increasing the radius of the reactor tube reduces the ratio of the heated area of the sample to its total reaction volume (S/V) which leads to considerably longer induction times and lower rates hydrogen generation (Fig. 1). To explain this result a mathematical model of the tubular reactor for the AB thermolysis has been proposed. It was shown that the model should include the dependence of the reaction rate on the reagent-product interface surface.

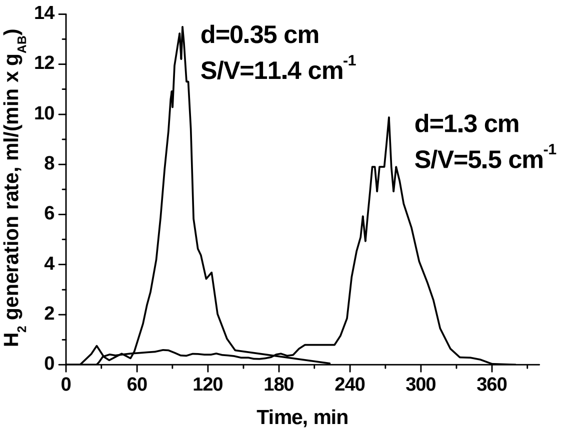

Fig. 1. Decomposition of «AB-Al» material depending on the reactor diameter (d) and the ratio of the heated area of the sample to its volume (S/V) at external heating of 90 °C

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PP-80

HYDROGEN STORAGE SYSTEMS BASED ON SOLID-STATE $NaBH_4$ COMPOSITES FOR HYDROGEN GENERATOR

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Hydrogen can be used directly in the proton exchange membrane fuel cells to generate electricity and water as a by-product. However, their efficient operation requires pure hydrogen desirably produced at ambient temperature (-40 ÷ +60 °C) with no supply of heat. Today, sodium borohydride ($NaBH_4$) is considered to be an efficient hydrogen storage material for small-scaled autonomous sources of energy. Aqueous-alkaline $NaBH_4$ solutions have been traditionally used as hydrogen sources but they tend to lose considerable amounts of hydrogen upon storage (to 40 % during 2 months). Therefore, it has been suggested that $NaBH_4$ should be stored in the form of solid composites - «hydrogen pellets» with added Co compounds [1,2] which have a high catalytic activity for $NaBH_4$ hydrolysis coupled with a reasonable price.

In this work the design of a hydrogen generator equipped with solid-state $NaBH_4$ composites (Fig. 1b) and its water supply system have been optimized (Fig.1a). To control the hydrogen generation process the effect of conditions used for the preparation of «hydrogen pellets» as well as of the reaction conditions on the rate of the $NaBH_4$ hydrolysis has been studied.

(a) **(b)**

Fig. 1. (a) «Hydrogen pellets» based on $NaBH_4$ and (b) hydrogen generator

«Hydrogen pellets» have an obvious advantage because of their high gravimetric hydrogen density (to 10 wt %). In addition to this, by decreasing the amount of water added to the solid composite it is possible to increase hydrogen capacity of the entire hydrogen generation system. In experiments with a pellet (0.06 g) of sodium borohydride with a cobalt catalyst, the amount of the added water had been decreased from 25 to 1 ml. It was found that in the range from 25 ml to 5 ml neither the yield of hydrogen nor the rate of its evolution had been affected. With further decrease in the content of water to 1 ml the rate of hydrogen generation begins to be limited by the dissolution of pellet in the small volume of water.

The kinetics of the gas generation was found to be zero order. Therefore by varying the content of the cobalt catalyst in the pellet it will be possible to obtain a desired rate of hydrogen generation.

Using a set of physicochemical methods (EXAFS, XPR, magnetic susceptibility, HR TEM), the formation of the catalytically active phase from the cobalt compounds in the solid $NaBH_4$ has been studied. It was found that the catalytically active phase begins to form already at the stage of pelletizing as a result of a solid-state interaction of $NaBH_4$ with the compounds of cobalt. The content of the active phase increases upon storage which explains the growth in the rate of hydrogen generation. Since some of $NaBH_4$ was used up for catalyst reduction its content was decreasing but the loss of hydrogen did not exceed 2.4 %. In the case when a pre-reduced catalyst had been added to the hydrogen pellet, the rate of hydrogen generation remained unchanged for half a year.

The performed studies have shown that solid-state $NaBH_4$ composites may prove to be an efficient alternative to the alkaline-aqueous solutions of $NaBH_4$ which have a low content of hydrogen.

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Acknowledgments

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PP-81

TECHNOLOGICAL SYNTHESIS OF OPTIMAL REACTOR SCHEMES FOR ISOMERIZATION PROCESS OF PENTANE-HEXANE FRACTION

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Russia's transition to production of high-quality motor fuels: EURO-4, EURO-5 standards with low content of aromatic hydrocarbons increased demand on isomerizate. This fact leads to necessity of exploitation technology of working isomerization unit improvement. One of the most efficient ways to deal with such complex problems of optimization reactor schemes is the mathematical modeling method on a physical and chemical basis.

Hypothetically generalized technological structure of the reactor block of isomerization process contains consistently connected reactors and columns for division of streams (fig. 1).

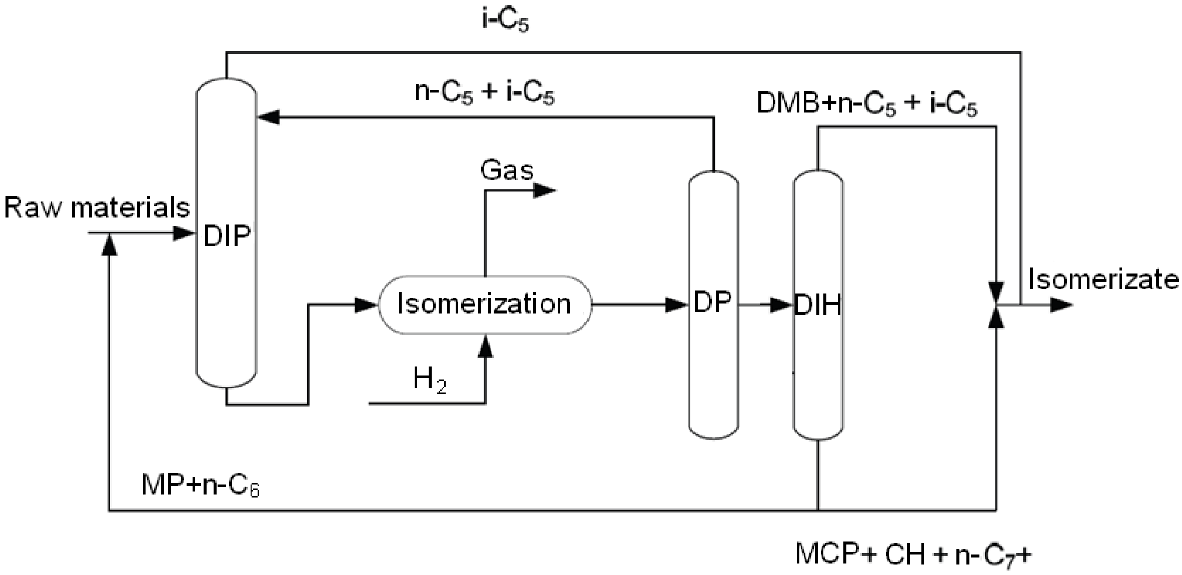

Fig. 1. Hypothetically generalized technological structure of the reactor block of isomerization process: DIP – Deisopentanization column, DP – Depentanization column, DIH – Deisohexanization column; MP – Methylpentane, DMB – Dimethylbutane, MCP – Methylcyclopentane, CH – Cyclohexane

Calculations using a mathematical model HYSYS - IZOMER [1] of isomerization process "Once-through", with two recycles of pentane and hexane, with one recycle of hexane realized (table 1).

Table 1 – Isomerizate compositions at the exit from the reactor block

Component	Technology of isomerization process		
	"Once-through"	With two recycles	With one recycle
n-C_4	0,16	0,42	0,44
i-C_4	0,13	0,00	0,06
n-C_5	14,14	0,00	11,56
i-C_5	32,97	2,32	30,96
n-C_6	5,94	6,86	0,54
2-Methylpentane	14,94	0,00	5,24
3-Mmethylpentane	7,60	9,86	0,76
2,2-Dimethylbutane	11,59	61,69	36,4
2,3-Dimethylbutane	4,36	14,89	5,24
n-C7	0,04	0,13	0,0
Sum i-C7	3,24	3,74	0,0
Sum C8	1,77	0,00	0,0
Cyclopentane	0,83	0,00	9,18
Methylcyclopentane	1,05	0,00	0,4

"Once-through" scheme is notable for the least capital and operating costs. This scheme makes it possible to produce isocomponent with RON 81 – 85. Isomerizate consists of large number such components as isopentane, isohexane.

Recycle of low-branched hexanes scheme allows increasing octane number of the produced isocomponent due to recycle of low-branched hexanes back to reactor section feed. In comparison with "once-through-run" scheme, this scheme includes additional deisohexanization column (DIH) and provides isocomponent with 87-88 RON. In composition of isomerizate the number of isohexane is increased because of removing low-branched hexanes.

N-pentane and low-branched hexanes recycle scheme allows maximum usage of technology capabilities in pentane-hexane fractions isomerization. Further equipping of isomerization unit scheme with feed deisopentanization column allows decreasing load on reactor section and increasing pentane isomerization depth. Iso-component octane number (91-92) is achieved due to n-pentane and hexanes recycle. Isomerizate consists of the most large number isohexane.

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KINETIC MODELING OF THE CATALYTIC KETONIZATION OF HEXANOIC ACID

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Catalytic ketonization of hexanoic acid was considered in the present study. Although most of kinetic studies have focused on the formation of 6-undecanone (UDO) directly from hexanoic acid (HA), there are some reported works where ketene, carboxylate salts, β-ketoacids, and acid anhydride have been suggested as an intermediate of the catalytic ketonization reaction [1-2]. In our previous work, hexanoic anhydride (HAn) had been experimentally observed as a reaction intermediate [3], and thus, the kinetic model composed of two steps is proposed in the present study: (step 1) the formation of a HAn by two HA's, which is followed by (step 2) the transformation of HAn to UDO as follows:

$$2C_5H_{11}COOH \leftrightarrow [CH_3(CH_2)_4CO]_2O + H_2O \quad (1)$$

$$[CH_3(CH_2)_4CO]_2O \leftrightarrow CH_3(CH_2)_4CO(CH_2)_4CH_3 + CO_2 \quad (2)$$

Experiments were conducted using zirconium oxide (ZrO_2) aerogel catalysts under various conditions; space velocity (4–14 h^{-1}), temperature (300–330 °C). In addition, feed was composed of both HA and HAn, and their composition were varied to clearly investigate the role of the intermediate in the kinetic pathways; HA/HAn (0.0/0.5/1.0/2.0).

Reaction rate were developed on the basis of the Langmuir-Hinshelwood mechanism under the assumption that the above two reactions (equations (1) and

(2)) take place reversibly, and the adsorption/desorption of chemical species are negligibly affected by temperature. Kinetic parameters were estimated by fitting experimental data, and the validity of the proposed model was corroborated by the comparison of simulated results with the observed data (mean of absolute relative residuals for HA and HAn conversion, and UDO yield were calculated 14.3 %, 8.8 %, and 18.4 %, respectively). The model clearly shows the contribution of HAn in the formation of UDO, and can be used in the determination of the optimal reaction condition to maximize the production of UDO.

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PYROLYSIS OF OIL-CONTAINING WASTE IN THE PRESENCE OF METAL CHLORIDES

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The main source of the heavy and residual hydrocarbons is the waste of oil crude refining. The world crude oil production increases every year and at present amounts to 49 billions tons per year. The oil-containing waste can be obtained at all the stages of processing, storage, transportation and the use of oil. It also requires the vast area for the earthen containers and sludge collectors, resulting in the energy carrier price rise [1].

The existing methods of oil-containing waste processing can be divided into physical, chemical, physicochemical, thermal and biological [2]. The choice of the method of oil-containing waste processing and decontamination mostly depends on the amount and nature of oil-products in oil-containing waste. The thermal treatment resulting in gaseous and liquid fuel formation is considered to be the most economically beneficial. Besides oil waste sensible utilization can be an essential step towards the development of resource-saving technology on the basis of the integrated use of oil raw material.

Catalytic pyrolysis of oil-containing waste allows obtaining hydrocarbons which can be used either as fuel or raw material for the chemical industry [3]. Compared to other methods of oil-containing waste thermal treatment, catalytic pyrolysis has a number of advantages: (i) rather low process temperatures (400-650 °C), (ii) low sensitivity to the raw material composition and (iii) a closed circuit of processing that comply with the modern requirements of chemical production.

In the present paper we report on the results of the process of heavy and residual hydrocarbons thermocatalytic processing with metals chlorides KCl, NaCl, $MgCl_2$, $AlCl_3$, $FeCl_2$, $FeCl_3$, $ZnCl_2$, $CoCl_2$ и $NiCl_2$. The pyrolysis process was carried out with an experimental pyrolysis set-up in a temperature range from 450 to 650 °C. The experimental pyrolysis set-up consists of a metal fixed-bed reactor heated with the electric furnace, a gas sampler, a water trap for collecting liquids, and a eudiometer for collecting gas.

The study of the kinetics of the oil sludge pyrolysis process was carried out using the thermoscales TG 209 F1 (NETZSCH) with different heating rate (1, 5, 10, 15 and

20 °C/min). The oil-containing waste samples with the amount of crude oil 20 % (wt.) without a catalyst and with 5 % (wt.) $CoCl_2$ were used for the analysis.

The influence of metals chlorides on the oil-containing waste thermal degradation is explained by two major factors: (i) strength of the catalyst aprotic acid sites and (ii) cation electronegativity.

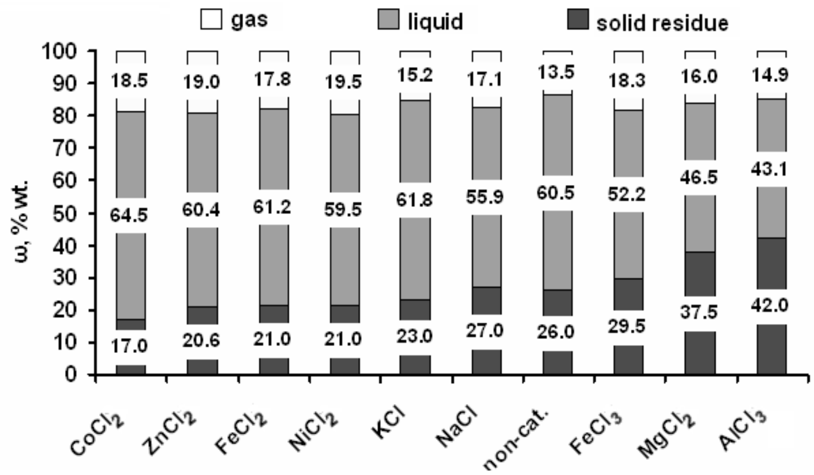

Figure – Dependence of pyrolysis product yields on the catalyst

Cobalt, zinc and nickel chlorides showed the highest catalytic activity in the oil-containing waste pyrolysis while the use of cobalt chloride resulted in the highest degree of conversion into gaseous and liquid products and allowed a 41.2 and 8.5 % (wt.) increase, respectively, compared to the non-catalytic process. In the presence of cobalt and nickel chlorides the volumes of the C_1-C_4 hydrocarbons increased by factors 2.4 and 2.9, respectively, compared to the non-catalytic process. Therefore, for the model oil-containing waste sample pyrolysis, we recommend catalytic process at 500 °C and at 5 % (wt.) of cobalt chloride of the oil-containing waste oil fraction weight.

The use of $CoCl_2$ in the oil-containing waste pyrolysis process leads to the change of the destruction mechanism and to the decrease in the process activation energy by 20-30 kJ/mol.

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PP-84

HYDROPROCESSES IN BIOFUEL SYNTHESIS

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The growing interest to renewable energy sources is caused by the decrease of petroleum sources, oil pricevolatility and environmental hazards [1]. Nowadays there are numeral investigations in the field of biofuels production focused on oils and fats processing. The processes of oils and fats conversion to biodiesel are mainly divided into two reactions: transestherification and hydrotreatment. Hydrotreatment is a group of reactions allowed obtaining biofuels with lower oxigen content in comparison of used raw material, also it allows using waste and non-eatable oils. This process includes such reactions as hydrogenation [2], hydrocracking, decarbonylation, decarboxylation etc. [3, 4]. All these reactions remain rather high temperature and hydrogen pressure, so to decrease the indicated parameters and therefore to decrease final product cost current investigations are focused on the search of stable, effective and non-sulfurized catalysts [5].

In this work two processes of fatty acids conversion using polymerstabilized catalysts based on noble metals were investigated. Stearic acid purchased by KhimMedServis (Russia) was chosen as a model compound for both hydrodeoxygenation and hydrogenation processes. Both processes were carried out in Parr Series 5000 Multiple Reactor System. Temperature was varied in the range of 150-250 °C in the case of stearic acid hydrogenation and 230-260 °C in the case of hydrodeoxygenation. Partial hydrogen pressure was set up to 2 MPa for hydrogenation and 0.6 MPa for hydrodeoxygenation processes. Novel polymerstabilized catalysts on the base of Pt subgroup metals impregnated to the matrix of hypercrosslinked polystyrene (HPS) were used as catalysts for hydrotreatment processes. Reactions were carried out in the media of n-dodecane.

The catalyst structure was studied using the following physico-chemical methods: low-temperature nitrogen physisorbtion, transmission electron mycroscopy, X-Ray photoelectron spectroscopy, IR-spectroscopy, thermogravimetric analysis. To analyze the liquid reaction phase composition GC-MS was used.

In the case of hydrodeoxygenation process the optimal parameters were found to be the folllowing: temperature – 255 °C, initial stearic acid concentration – 0.1 mol/L, mass of catalyst 0.1 g. The most effective catalytic system allowed acheaving the highest selectivity (99 %) of target product – n-heptadecane – was found to be 1 %-Pd/HPS. The stearic acid conversion reached up 100 %.

To obtain the highest yield of target product of hydrogenation reaction – stearyl alcohol the temperature was found to be 200 °C, initial substrate concentration – 0.1 mol/L, mass of catalyst – 0.1 g. While using 1 %-Pd/HPS the selectivity regarding to stearil alcohol was obtained equal to 93 % an 100 % substrate conversion.

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PP-85

MAKING CHEMICALS FROM SUNLIGHT: REACTOR EVALUATION AND KINETIC ANALYSIS IN A SPINNING MESH DISC REACTOR

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IChemE 21st century roadmap states: “we must continually reassess our approach to plant design and the acceptance of innovative concepts to render the chemical industry sustainable”. Photocatalysis is an alternative method of capturing and using energy and in particular, solar light catalysed reactions are a growing and vibrant research area. One innovative path for a future sustainable and competitive chemical Industry is thus to use sunlight to synthesize chemicals. Imines are valuable intermediates in the pharmaceutical industry, as well as in organic synthesis, with the C=N bond frequently being exploited for its reactivity [1]. In order to increase the efficiency of the process and to reduce waste, significant effort has been put in to developing one-pot oxidative reactions of amines to imines [1]. This work investigates a solar-photocatalytic method for the homo-coupling of amines to form the corresponding imine comparing batch, microflow and spinning disc reactors using a range of light intensities, reaction conditions and light simulation systems.

The effect of catalyst and substrate concentration was firstly evaluated using a standard 50 W LED light source using stirred and non-stirred batch reactors. The reaction was monitored taking discrete NMR samples (using solvent suppression) and Flow NMR. The influence of reactant and catalyst concentration, temperature, surface area, reaction volume on conversion and reaction rate were investigated. The results show that an increase in temperature, surface area, substrate concentration increases the reaction rate, whilst decreasing the reaction volume increases the reaction rate. Increasing the catalyst concertation decreased the reaction rate, which is likely due to the darker solution affecting light penetration. Stirring had no effect on reaction rate indicating that light intensity was the limiting factor and not mass transfer. Discrete samples resulted in first order rate constants between $5\text{-}6{\cdot}10^{-5}$ s^{-1} and flow NMR gave a similar 1st order rate constant of $4{\cdot}10^{-5}$ s^{-1}.

The second set of experiments were carried out using a novel solar-light set-up (specially designed by SunTech Group AB, Sweden) which allows a range of solar intensities between 400-1200 W. Initial experiments reduced the time from about 24 h for completion to less than one hour, and a 1st order reaction rate constant around $1{\cdot}10^{-3}$ s^{-1} and these results are likely mass transfer limited, further confirming that light intensity is the most important factor.

One reactor technology that can produce thin films (to maximise light penetration), that allow for immobilization of catalyst and achieves high mass transfer is the spinning mesh disc reactor [2, 3]. It consist of a rotating disc with a cloth resting on top and a jet of liquid impinging onto the centre of its top surface. The centrifugal force of the spinning disc forces this liquid to form a thin and highly sheared film on top of the rotating surface, significantly increasing the heat and mass transfer and it has also been shown to increase the photonic efficiency in comparison to annular reactors [4]. Experiments are currently being run in a spinning mesh disc reactor and preliminary results are showing that process intensification is occurring with flowrate being more important than spinning speed in terms of reaction conversion for both free and immobilized Eosin Y.

In conclusion, we have evaluated a range of conditions that both characterise and optimise a solar light Eosin Y catalysed reaction. We have furthermore applied this reaction in a spinning disc reactor and achieved significantly faster reaction rates. Future work is focussing on changing from homo to hetro coupling and comparing the reaction system to microreactors.

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PP-86

DYNAMICS OF SOOT PARTITIONING BETWEEN ONE TRAPPED INSIDE THE POROUS WALLS AND ON THE SURFACE OF DIESEL PARTICULATE FILTERS

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Particulate matter (PM) from Diesel engine exhaust consists of solid carbon (soot) and unburned carbonaceous compounds. PM is one of the main air pollutants. Wall flow Diesel particulate filters (DPFs) are being extensively used for removal of PM from exhaust gas. The exhaust gas flows through the porous walls from the inlet channel of DPF into the outlet one. Computer modelling and simulation are widely used to predict the operation conditions of DPFs. It both allows to reduce testing costs and offers a better understanding of the underlying phenomena. Different scale sub-models, e.g., the channel wall sub-model and the soot layer on the wall surface one are at present solved separately and on the assumption of a single particle size.

The paper is devoted to the simultaneous modelling and simulation of soot trapping inside the porous walls of the filter and on the surface of the walls (soot cake). A particulate size distribution effect is also taken into account for the modeling.

Model equations and boundary conditions are given below:

$$\varepsilon\frac{\partial c_j^{soot}}{\partial t}+v\frac{\partial c_j^{soot}}{\partial x}=-v\cdot\varphi\cdot\eta_j\cdot c_j^{soot},\ j=1,N \qquad (1)$$

$$\frac{\partial m_j}{\partial t}=v\cdot\varphi\cdot\eta_j\cdot c_j^{soot},\ j=1,N;\ m=\sum\nolimits_{j=1}^{N}m_j \qquad (2)$$

$$h_{cake}=\left(\int_0^t\sum\nolimits_{j=1}^{N}\left(c_{j\,in}^{soot}-c_{j\,out}^{soot}\right)\cdot v\cdot dt+\int_0^L\left(\sum\nolimits_{j=1}^{N}c_{j\,out}^{soot}+m\right)\cdot dx\right)/\rho_{soot} \qquad (3)$$

$$\Delta P=\frac{v}{S}\cdot\mu\cdot\left[K_{cake}\frac{(1-\varepsilon_{cake})^2}{d_{cake}^2\cdot\varepsilon_{cake}^3}h_{cake}+K_w\int\limits_0^L\frac{1}{d_w^2}\cdot\frac{(1-\varepsilon_w)^2}{\varepsilon_w^3}dx\right] \qquad (4)$$

$$\text{x=0:}\ c_{j\,in}^{soot}(0,t)=\left(c_{in}^{soot}/\sqrt{2\pi}\,\ln\sigma_p\right)\exp\left[-0,5\left(\left(\ln d_p^j-\ln\mu_p\right)/\ln\sigma_p\right)^2\right],\ j=1,N \qquad (5)$$

$$t=0:m(x,0)=0,\ c_j^{soot}(x,0)=0,\ j=1,N \qquad (6)$$

Equations (1) describe the concentration c_j^{soot} of soot particles of *j-th* sizes in gas phase inside the pores of the filter walls. Equation (2) describes the concentration m of soot particles of all sizes, accumulated inside the pores of the filter walls. Equations (3) and (4) calculate the thickness of soot cake h_{cake} and pressure drop ΔP across the wall and the cake upon it, correspondingly. Filtration efficiency in the walls η_j depends on several mechanisms, namely, inertial impaction, interception, Brownian diffusion and interactions between interception and Brownian diffusion. We allow for soot collection on the wall surface by inertial impaction, after the soot amount on the surface or inside the wall exceeds a critical level ($h_{cake}^{\max}$ or $m^{\max}$) all soot deposits on the surface. η_j depends on the particle size $\mathrm{d}_\mathrm{p}^\mathrm{j}, j=1,N$, gas velocity v and the wall structure, namely, pore diameter d_w, porosity ε_w and fiber diameter d_f, which, in turn, depend on accumulated soot. For the description of poly-dispersed solid-gas flow, real soot distribution (5) is substituted by a series N of mono-dispersed particles distributions. We present the modelling results for different wall materials and particulate size distribution from Opel exhaust in Figure 1. The material properties of fiber quartz and SiC are: ε_w = 0.86, d_w = 10 μm, d_f = 4.4 μm and ε_w = 0.37, d_w = 10.3 μm, d_f = 10.2 μm, respectively. $m^{\max} = \rho_{soot} \cdot \varepsilon_w$.

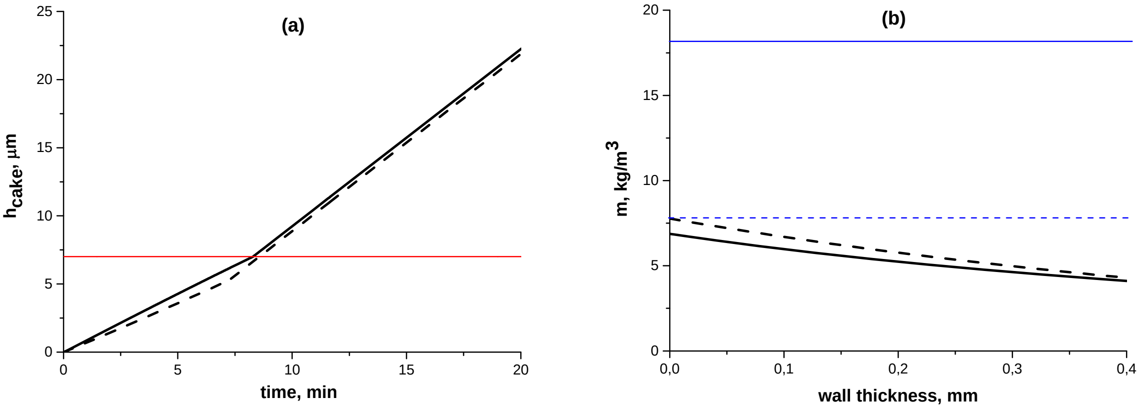

Fig. 1. Growth of the cake's thickness with time (a), accumulated soot profiles at time when critical level is obtained ($h_{cake}^{\max}$ or $m^{\max}$) (b) for different wall materials. Solid black lines – fiber quartz, dash black lines – SiC, red line – $h_{cake}^{\max}$, solid blue line – $m^{\max}$ for fiber quartz, dash blue line – $m^{\max}$ for SiC

For dense SiC all soot deposits on the surface when $m = m^{\max}$ (t = 7.2 min). For fiber quartz with large porosity all soot deposits on the surface when $h_{cake} = h_{cake}^{\max}$ (t = 8.2 min). Simultaneous modelling of soot trapping inside the walls and on its surface and including soot size distribution effect will permit to correctly compute the performance of DPFs and predict the operation conditions.

Nomenclature

φ - depth of the particle penetration into the walls; ρ_{soot} - bulk soot density; S - surface area; K - coefficient; μ - gas viscosity; μ_p - media particle diameter; σ_p - standard deviation of particle size distribution; L - wall thickness; x - wall coordinate; t - time; indexes: $_{\mathrm{cake}}$ - soot layer on the wall surface; $_{\mathrm{w}}$ - wall; $_{\mathrm{in}}$ - wall coordinate, x =0; $_{out}$ - wall coordinate, x = L.

PP-87

KINETICS OF PERACETIC ACID SYNTHESIS IN THE CONTINUOUS FLOW REACTOR

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Peracetic acid (AcOOH) is widely used in everyday life (bleach, disinfectants) and in the industry as an epoxidizing agent [1]. Currently, it is obtained from standard solutions of acetic acid (AcOH) and hydrogen peroxide (H_2O_2) in the presence of acid catalyst (sulfuric acid, cation exchange resin). However, the use of sulfuric acid is accompanied with severe corrosion of equipment and the use of cation exchange resins with vigorous stirring leads to mechanical wear and loss of its catalytic properties.

In the last few years it has caused a genuine interest among researchers of the process in the flow reactor with a fixed bed catalyst [2, 3]. It is increased catalyst life by reducing its mechanical wear in this reactor. But the detailed work on the kinetics and mechanism of the formation of acetic acid does not allow providing comparative analysis of data homogeneneous and heterogeneous catalytic process, because it is difficult to find a comparable process conditions. Discussion remains on the question of the ways of the decomposition of active oxygen.

Therefore, the aim of this study was to compare the kinetic data on the synthesis of peracetic acid in batch and continuous conditions, as well as the identification of kinetics of the process in a flow reactor with a fixed bed catalyst – cation exchange resin.

Analysis of the material balances of active oxygen ($C(H_2O_2)_i+C(AcOOH)_i$) and the total acid ($C(AcOH)_i+C(AcOOH)_i$) showed that the concentration of active oxygen is reduced due to consecutive reaction of peracetic acid bimolecular decomposition to molecular oxygen (Fig. 1). The rate of decomposition reaction is reduced with increasing concentration of the catalyst.

A key factor influencing the synthesis of peracids in continuous reactor is the presence of diffusion processes at the "liquid – solid" interface. Thus, at low feed rate there is a linear decrease in balance of total acid, whereas the balance of acid is constant with increase of feed rate (Fig. 2).

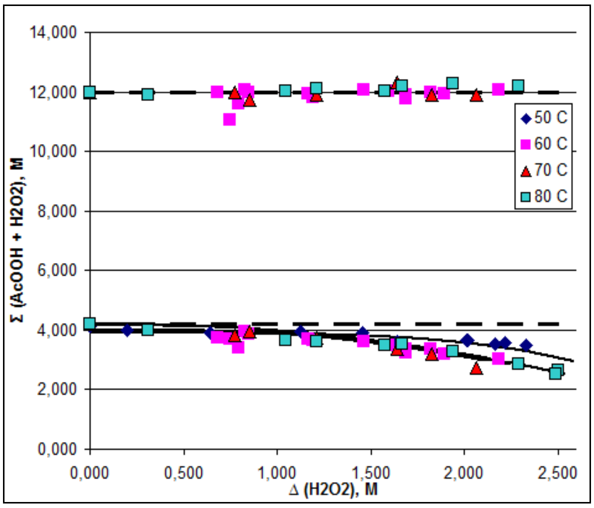

Fig. 1. Correlation of sum current concentrations {[AcOH]$_i$ + [AcOOH]$_i$} and {[H_2O_2]$_i$ + [AcOOH]$_i$} and the current hydrogen peroxide concentration ([H_2O_2]$_0$ - [H_2O_2]$_i$) for reactions conducted in the temperature range 50-80 °C (initial concentration of hydrogen peroxide and acetic acid 4 and 12 M, respectively). Lines represent the calculated data

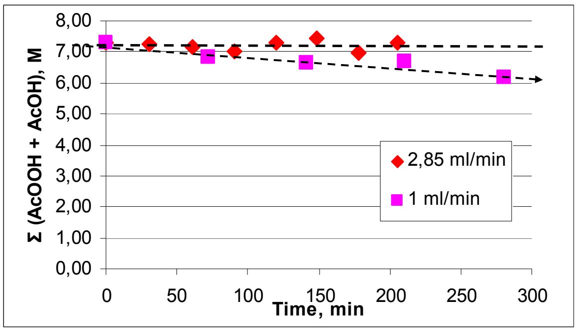

Fig. 2. Balance of total acid versus time for different feed rates (initial concentration of hydrogen peroxide and acetic acid both 7.3 M, respectively)

The degree of saturation of the catalyst prior to synthesis affects on the formation of peracetic acid. It was found, that the saturation of the catalyst Amberlyst 15 Dry water leads to equilibrium concentration of peracid one and a half times less then in the case of acetic acid saturation under the same conditions (initial concentration of hydrogen peroxide and acetic acid both 7.3 M, respectively, T = 50 °C, feed rate – 4 ml/min). This fact supports the hypothesis competitive adsorption of reactants on the catalyst surface, resulting in a significant disequilibrium in the system.

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IN SITU EPR STUDY ON REDOX PROPERTIES OF $CuO-CeO_2$

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Understanding the redox properties of metal oxide based catalysts is a major task in catalysis research. With time dependent *in situ* studies the change of metal ion valences and formation of active sites during redox reactions can be observed directly, and thus help unveil the ongoing redox pathways[1-4]. Here *in situ* Electron Paramagnetic Resonance (EPR) spectroscopy combined with online gas analysis and mass spectrometry, *ex situ* X-ray photoelectron spectroscopy, X-ray diffraction, temporal analysis of products reactor studies, was utilized to study the redox behavior of $CuO–CeO_2$ catalysts under PROX conditions (preferential oxidation of carbon monoxide in hydrogen). From these measurements a *synergistic mechanism*, involving the redox pair Ce^{4+}/Ce^{3+} during oxidation of Cu^0/Cu^+ species to Cu^{2+}, and a *direct mechanism* that bypasses the redox pair Ce^{4+}/Ce^{3+} could be distinguished. In addition, a quantitative evaluation of the Cu^{2+} EPR intensities upon / during reduction under CO and oxidation under O_2 revealed that the *synergistic mechanism* represents the major reaction pathway during the PROX reaction. Strong interactions between Cu and Ce accordingly would lead to a better catalytic performance. With this guideline, the $CuO-CeO_2$ catalyst was optimized to have a wide temperature operation window of 11 degrees, ranging from 377 K to 388 K, with 99 % conversion and 99% selectivity, in the preferential oxidation of CO in a H_2 feed.

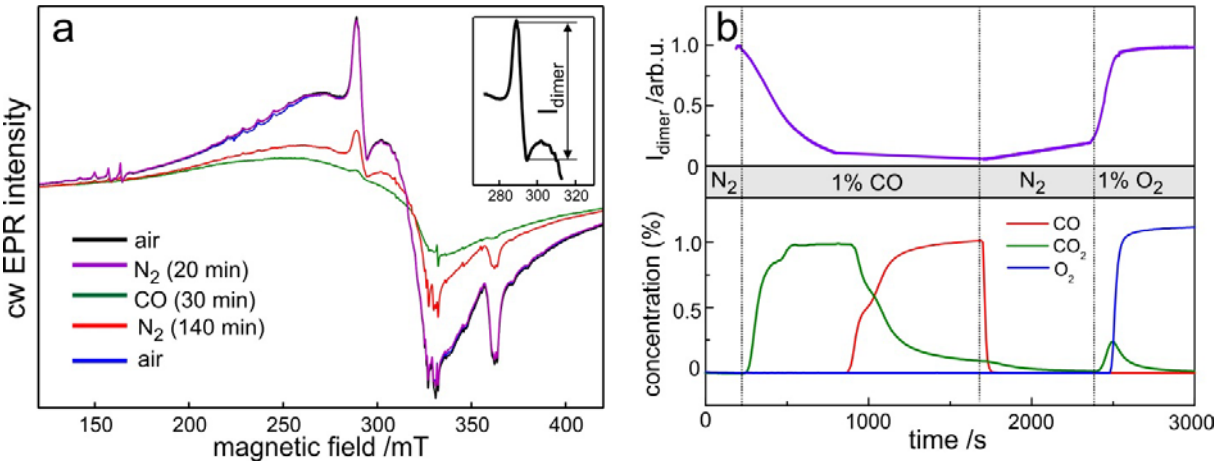

Figure 1. Identification of *synergistic mechanism*. (a) X-band cw EPR spectra of 20 wt % CuO-CeO_2 recorded at 453 K during the treatment with air/N_2/CO/N_2/air. The durations of the particular gas treatment are indicated. The insert shows the dimer EPR signal used for kinetic measurements. (b) Upper trace: Time dependence of Cu^{2+} dimer EPR intensity at 289 mT during N_2/CO/N_2/air cycle at 453 K. Lower traces: Corresponding CO, CO_2 and O_2 concentration simultaneously recorded by gas analytic system. Oxidation of Cu^0/Cu^+ species to Cu^{2+} is observed under pure N_2, which is the indication that Ce^{4+}/Ce^{3+} participates the reaction.

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PATTERN FORMATION IN PULSED GAS-SOLID FLUIDIZED BED REACTOR – A COMPUTATIONAL STUDY

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Bubbling gas-solid fluidized beds are widely employed in various industrial processes in which increased interfacial heat and mass transfer are essential, such as drying of powders, solid fuel or waste combustion, fluid catalytic cracking and gasification.

Overall process performance is strongly dependent on the bubble dynamics, which are complex. Bubbles grow while rising through the bed along irregular trajectories with possible coalesce and breakups, driving the chaotic solids circulation conjunctly, which obscures greatly the operation, design and the scale-up of fluidized bed reactors [1].

Introducing additional degrees of freedom makes it possible to manipulate the bubble dynamics. In particular, it has been shown that gas-solid fluidized beds can form remarkably regular dynamical patterns when subject to an external pulsated gas flow under certain experimental conditions [2, 3], which can be employed as a method to structure the hydrodynamics. In quasi-2D bubbling beds, bubbles rise forming hexagonal configurations, alternating their position at every pulse. In shallow 3D beds, the top surface displays regularly organised stripes and squares, resembling patterns observed in vibrated granular media [4].

Interestingly, this striking visual manifestation tied to the complexity of the underlying physics make pattern formation excel as a validation tool for computational fluid dynamics (CFD) models, as discussed in a recent article [5]. Over the last two decades, CFD codes of varying complexity have been implemented to study fluidized bed reactors in an academic and industrial context. One difficulty, however, is that the more detailed models that explicitly simulate individual particle trajectories are unable to be used to simulate large-scale processes, while less detailed, averaged two-fluid models include approximations that might not sufficiently account for the physics of granular matter.

Granular media are commonly described at two different scales, namely by local averaging and individual tracking. Both can predict various fluidization behaviors satisfactorily. However, so far, CFD has not been able to show convincing agreement with the regular pattern of bubbles observed experimentally [6].

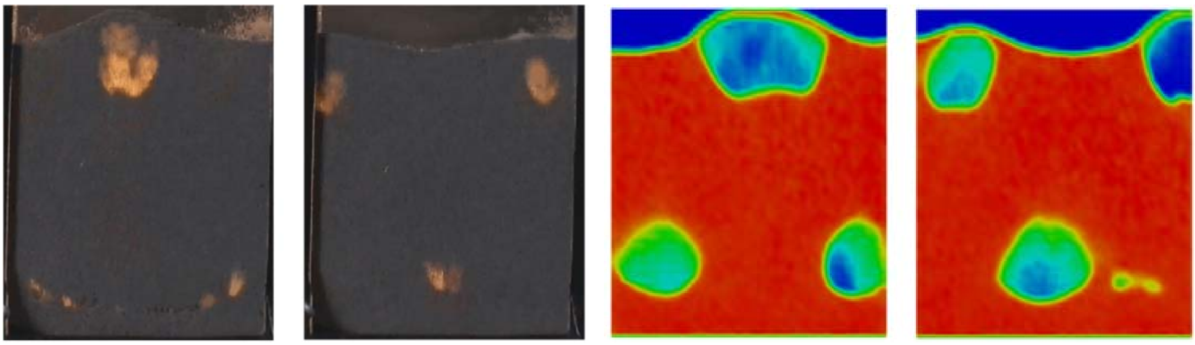
(a) (b)

Figure 1. Snapshots of (a) experimental and (b) simulated (using a discrete element model, DEM-CFD) bubble patterns in a 15 cm x 15 cm quasi-2D pulsed fluidized bed. The snapshots were taken from two consecutive periods of the oscillating gas flow for both experimental and simulated patterns. Superficial inlet velocity, $U_0/U_{mf} = 1.4 + 0.5\sin(2\pi 4t)$; particle size = 450 μm; minimum fluidization velocity (U_{mf}) = 0.14 m/s

In this contribution, we present the first successful simulations of experimentally witnessed patterns in gas-solid fluidized beds, as shown in Figure 1, and discuss our last insights about pattern formation by studying the bed dynamics computationally during a patterned state. Our discrete element modeling approach correctly reproduces the bubble pattern, whereas the two-fluid approach fails, suggesting an important role of solid mechanics for inducing the pattern formation.

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PP-90

CALCULATION OF PR-9 CATALYST CHARACTERISTICS UNDER REDUCED PRESSURE IN THE REFORMING UNIT INDUSTRIAL REACTOR

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Catalytic naphtha reforming is one of the key processes in the petroleum refining and petrochemical industries, which is used extensively to convert low-octane hydrocarbons of naphtha to more valuable high-octane gasoline components without changing the boiling point range [1]. The strategy of reforming technology improving goes hand in hand with a pressure reduction. However, with the pressure decreasing the coke deposition on the catalyst and the catalyst deactivation rate increase. For this reason, the reforming process with a fixed bed catalyst is not carried out at a pressure lower than 1.4-1.5 MPa. Catalytic reforming unit L-35-11/450K with a preliminary hydrotreating is an important subject of "Komsomolsk Refinery" JSC in the Far East of Russia. Previous foreign catalyst charge PR-9 («Criterion» company) has proven to be appropriate in operation and ensure high specified quality yield. With a mathematical model using the pressure effect on the product yield and quality was analyzed [2]. The results of chromatographic analysis of the hydrocarbon feedstock composition, technological modes of production unit operation were used as source data. Figures 1, 2 and Table 1 show the results.

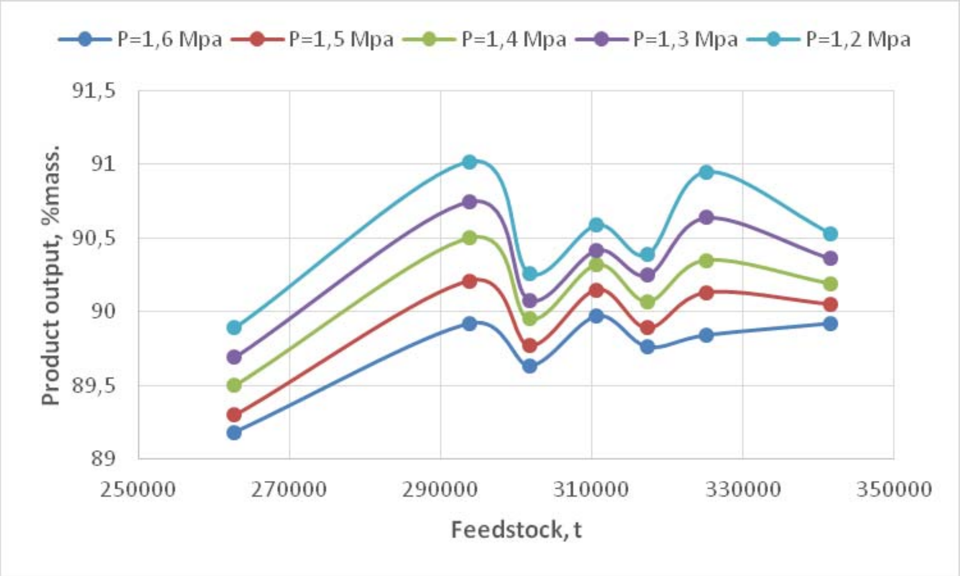

Fig. 1. The product yield on the catalyst under reduced pressure in relation to the feedstock

The figures below show the gradual increase of the product yield (Fig. 1, Table 1) on 1-2 % mass. with gradual pressure decreasing. In the coke accumulation dynamics (Fig. 2, Table 1), on the contrary, there are no significant changes were observed. This is due to the fact that pressure decreasing increases coke formation in the reactor according to the Le Chatelier's principle, but an additional amount of chlorine and water feed to the reaction zone compensates and reduces the coking rate (Table 1).

Table 1. The main PR-9 catalyst characteristics under reduced pressure

Pressure, kg/cm^2	**P=16**	**P=15**	**P=14**	**P=13**	**P=12**
Octane number (RON)	93,2	93,4	93,6	93,7	93,8
Aromatics, %mass.	60,66	61,01	61,32	61,56	61,81
Hydrogen output, %	1,94	1,97	2,0	2,04	2,07
Coke, %mass.	3,63	3,69	3,67	3,64	3,62
Product output, %mass.	89,92	90,05	90,19	90,36	90,53

Thus, the operating pressure deacreasing of the reforming process promotes its selectivity, favors the naphthenes dehydrogenation and paraffins dehydrocyclization reactions, and hydrocracking and hydrogenolysis side reactions inhibiting. Herewith the gasoline yield and hydrogen increases.

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PP-91

HIGH PURITY PRODUCTION OF FERRITES IN A PYROLIZER FOR BUTADIENE PRODUCTION

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The pyrolizing system is a simple process to make catalyst than co-precipitation. After pyrolysis of catalyst solution, catalyst powder is collected in a heating chamber. The impurities such as nitrate salts even react with air to produce NO_x and H_2O in a heating chamber, and is resulted in high purity catalyst. This efficient method enhances the catalytic performance in the oxidative dehydrogenation of n-butenes to 1,3-butadiene. Ferrite catalysts prepared in this manner, with adding transition metals to ferrite, is proven to be effective in catalytic activity. Also, the structure formation of catalysts were comfirmed by XRD.

MATHEMATICAL MODELING OF OXIDATIVE REGENERATION OF THE CATALYST FOR HYDROTREATMENT OF DIESEL FUEL

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The regeneration of spent catalysts is an important stage in the processes of oil refining and petrochemistry both for moving and fixed catalyst beds [1]. The oxidative regeneration based on oxidation of coke with oxygen is the most effective way to remove coke deposits among the known regeneration processes. Taking into account moderate thermostability of the most catalysts used in oil refining and petrochemistry (the maximum temperatures during the process should not exceed 450–650 °C, depending of catalyst type) and strongly exothermal character of oxidation reactions, there are inexorable demands for thermal regimes of oxidative regeneration. This study is dedicated to more detailed analysis of oxidative regeneration of $Co\text{-}Mo/Al_2O_3$ catalyst for hydrotreatment of diesel fuel by means of mathematical modelling.

It is assumed the following stoichiometric schemes of proceeding of oxidation reactions during the regeneration (for molybdenum and cobalt sulfides and coke):

$$MoS_2 + 3.5\ O_2 \Rightarrow MoO_3 + 2\ SO_2 \qquad (1)$$

$$CoS_{0.89} + 1.39\ O_2 \Rightarrow CoO + 0.89\ SO_2 \qquad (2)$$

$$C + O_2 \Rightarrow CO_2 \qquad (3)$$

Kinetics of oxidation reactions was studied by TG-DTA-MS (thermogravimetry – differential thermal analysis – mass spectroscopy) method, using the Netzsch STA 409 PC device connected with SRS UGA 200 mass spectrometer. Experiments included the programmed temperature rise of the catalyst powder (0.25-0.5 mm) from 50 to 450 °C (with temperature ramp 1 or 3 °C per minute) in the argon/-oxygen media (oxygen content 4 and 10 % vol.). It was found that the rates of reactions (1-3) may be described by the common equation

$$\frac{d\theta}{dt} = -k_0 \exp(-\frac{E}{RT})\ \theta^n\ C_{O2}^m \qquad (4)$$

where θ – relative mass content of the corresponding surface component at the catalyst, k_0 – pre-exponent, E – activation energy, T – temperature, C_{O2} – oxygen conent. The best description of the experimental data was obtained for the following values of kinetic parameters: reactions (1) and (2) – $\ln k_0$ = 12.41 s^{-1}, E/R = 10108 K; reaction (3) – $\ln k_0$ = 10.55 s^{-1}, E/R = 11279 K. Reaction rate orders were equal to 1 for surface compound (*n*) and ~0.5 for oxygen (*m*).

The mathematical model describing regeneration took into account mass and heat transfer as between gas flow and pellet outer surface as inside the pellet pores, heat release during the reactions (1)–(3) and thermal conductivity of the bed.

To simulate different conditions of the regeneration the inlet gas flow contained varying oxygen content from 2 to 21 vol % and had the temperature 400 °C. Fig. 1 shows the coke content (a) and bed temperature (b) depending on bed length in different time moments for 4 vol % of oxygen in inlet gas flow. Initially was supposed the catalyst contains 11 wt % of coke. It can be seen that the bed temperature rises up to 1100 °C, that is harmful for catalyst.

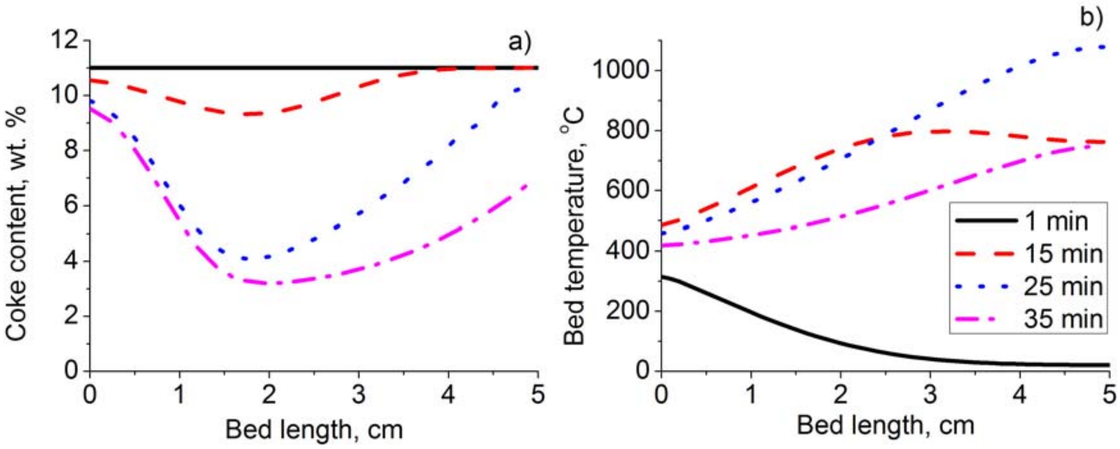

Fig. 1. Coke content (a) and bed temperature (b) in different time moments

The simulation showed that maximum temperature in the bed depends considerably on concentration of oxygen in fed mixture. So, this is exactly the parameter that may be used for thermal management of oxidative regeneration.

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ENHANCEMENT OF THE ACETYLENE YIELD FROM METHANE BY PARTIALLY DECOUPLING THE OXIDATION AND PYROLYSIS REACTIONS

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The partial oxidation (POX) of methane is the main approach to produce acetylene [1]. The reaction pathway analysis indicates that the exothermal oxidation reactions and the endothermic pyrolysis reactions are highly coupled in the POX process and thus the maximum yield of acetylene is limited to 33 %. This value cannot be further enhanced by optimizing the operating parameters [2]. A new process called partially decoupled method has been proposed and verified in this work. This process physically decoupled the oxidation and pyrolysis reactions. This method prevents methane from directly contacting with the strongly oxidizing groups and thus weakens the CO formation pathway (see Figure 1). The theoretical calculations based on the assumption of instantaneous and inert mixing of the heat carrier gas and methane shows that the maximum yield of acetylene can be enhanced to 52 %.

A jet-in-cross-flow (JICF) reactor is designed to realize this new process. This type of reactor has been successfully applied in the production of ethylene [3]. Computational fluid dynamics (CFD) simulations coupled with detailed chemical mechanism are used to investigate the influence of turbulent flow and turbulence-chemistry interaction. A modified GRI 3.0 mechanism [2], which has been verified by experimental data, is used in the simulations. The CFD model coupled with modified GRI 3.0 has been verified by simulating the original POX process. Figure 2 shows that the maximum acetylene yield of the new process can reach 42 %, which is much higher than that of the original POX process. The influence of the reactor structure parameters and operating parameters have also been investigated. The optimum nozzle number is 8 and the maximum acetylene yield decreases with the increase of diameter of the reactors. The optimum mixing ratio is 1750 K.

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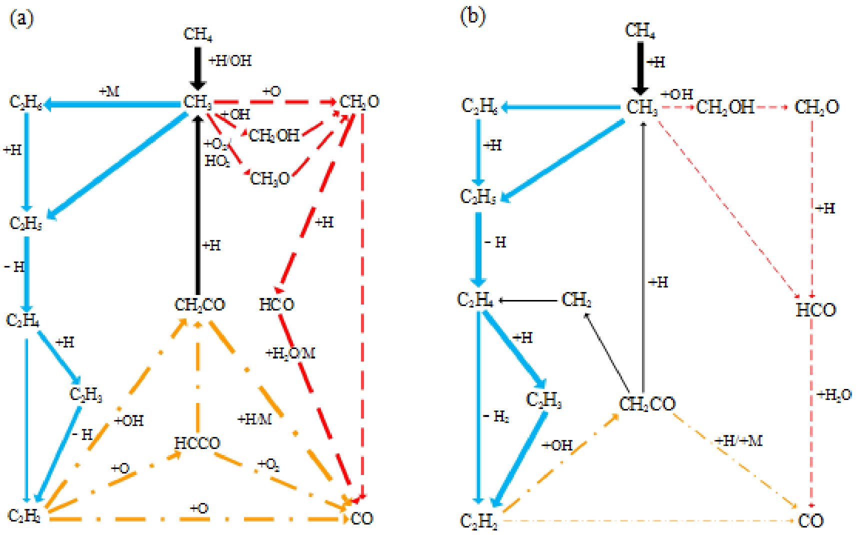

Figure 1. Simplified reaction pathways of acetylene and CO formation for (a) the original POX process before oxygen is exhausted and (b) the partially decoupled process

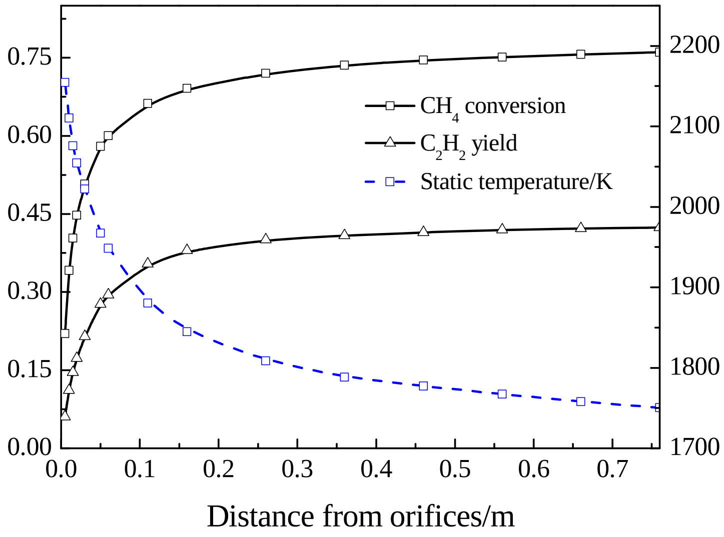

Figure 2. Simulated axial profiles of the mass-averaged static temperature, CH_4 conversion and C_2H_2 along the centerline of the partially decoupled process

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PRODUCTION OF METHYLETHYLKETONE BY OXIDATION OF N-BUTENE: WORKING OUT A METHOD FOR PRODUCING ENLARGED PARTY OF THE HOMOGENEOUS CATALYST (Pd + HETEROPOLY ACID) FOR THE PILOT TESTS

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Methylethylketone (MEK) is an organic solvent widely used in many industries. We suggested a method of MEK production by the direct catalytic oxidation of *n*-butenes with oxygen via reaction (1) [1].

$$n\text{-}C_4H_8 + {}^{1}/_{2}\,O_2 \xrightarrow{\text{Pd(II) + HPA}} CH_3COC_2H_5 \qquad (1)$$

Aqueous solutions containing Pd(II) complex and Mo-V-P heteropoly acids (HPAs) are used as catalysts for MEK-process, in which HPAs are reversible oxidants. In the catalytic process (1), the vanadium(V) atoms undergo redox transformations ($V^{V} \leftrightarrow V^{IV}$).

Reaction (1) is performed via two stages (2) and (3) which are accomplished in *two* different reactors **1** and **2**, respectively.

$${}^{m}/_{2}\ n\text{-}C_4H_8 + HPA + {}^{m}/_{2}\ H_2O \xrightarrow{Pd^{2+}} {}^{m}/_{2}\ CH_3COC_2H_5 + H_mHPA \qquad (2)$$

$$H_mHPA + {}^{m}/_{4}\ O_2 \longrightarrow HPA + {}^{m}/_{2}\ H_2O \qquad (3)$$

Such two-staged method excludes the direct contact between n-C_4H_8 and O_2 and permits to obtain high selectivity (97-98 %) in target reaction (2) at 60 °C. After reaction (2) in a butylene reactor **1**, MEK is distilled off from the reduced catalyst (Pd + H_mHPA) in a film evaporator. Next the catalyst is regenerated at 160 °C and P_{O_2} = 2-4 bar in an air reactor **2** via reaction (3) and again used in reaction (2). Consequently, reactions (2) and (3) compose the *catalytic cycle* of reaction (1).

We have proposed to use the HPA-7 ($H_{12}P_3Mo_{18}V_7O_{85}$) solution of *non-Keggin-type* as a basis of the (Pd + HPA) catalyst in MEK-process [1]. The HPA-7 solution has high thermal stability (up to 180 °C) and therefore can be fast regenerated at elevated temperatures (160–170 °C) without decomposition.

Kinetic peculiarities of the catalyst regeneration (3) were studied in our previous work [2], while the kinetics of target reaction (2) was investigated in [3]. These kinetic data were used for calculation and creation of a plug flow butylene reactor **1** and a perfect-mixing air reactor **2** in a pilot plant for the MEK-process. The technological scheme of this plant was shown and discussed in our work [3]. According to this scheme, the catalyst solution was moved in a closed cycle: the butylene reactor **1**, the film evaporator, the air reactor**,** and again reactor **1**. For the pilot test, it was required 1350 L of the catalyst.

We have developed a method of obtaining a pilot lot of the (Pd + HPA) catalyst with a total volume of 50 L [4]. The unit for the synthesis of one lot of the catalyst consisted of four stainless steel reactors with titanium blade stirrers. The 0.25 M HPA-7 solution was synthesized in several steps starting from V_2O_5, MoO_3 and H_3PO_4 by the overall reaction (4):

$$3{,}5\ V_2O_5 + 18\ MoO_3 + 3\ H_3PO_4 + 1{,}5\ H_2O \longrightarrow H_{12}P_3Mo_{18}V_7O_{85} \qquad (4)$$

The key point of the synthesis was dissolving V_2O_5 while stirring in a dilute and cooled H_2O_2 solution. The formed V(V) peroxide complexes decomposed at elevated temperature to give a 0.0175 M $H_6V_{10}O_{28}$ solution. This solution was stabilized by adding a calculated amount of H_3PO_4 to give a more stable 0.0125 M $H_9PV_{14}O_{42}$ solution. Since this solution occupied a large volume, its synthesis was performed three times in a 300-L reactor. In the main 500-L reactor, MoO_3 was dissolved in water with stirring, while adding the remaining portion of H_3PO_4. The resulting mixture was evaporated, gradually introducing all of the previously obtained portions of the dilute $H_9PV_{14}O_{42}$ solution. The resulting HPA-7 solution was evaporated to ~100 L and filtered twice, separating the insignificant amount of the precipitate. The filtered solution was again evaporated to 50 L, and a calculated amount of $PdCl_2$ was added to it while stirring at 70-80 °C. Repeating this procedure 27 times, a total lot of the (Pd + 0.25 M HPA-7) catalyst with volume of 1350 L was obtained. All apparatuses of the pilot industrial unit for MEK synthesis were filled with this catalyst.

The method for the preparation of a large batch of non-Keggin 0.25 M aqueous HPA-7 solution [4] seems promising not only for the industrial MEK synthesis, but also for a wide range of other oxidative processes involving Mo–V–P HPA solutions.

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DEVELOPMENT, CONTROL AND MODELLING OF A SCALABLE CONTINUOUS MANUFACTURING PROCESS FOR MULTIPHASE OXIDATIONS

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In the production of pharmaceuticals and fine chemicals, most reactions are conducted 'homogeneously' in one phase, and typically requires additional operations (known as 'work up') to separate the product from byproducts and any remaining starting materials and catalysts at the end of the reaction. Work up/separation procedures can be complicated and time-consuming, and can constitute 40-70 % of the costs of chemical processes. They also consume additional resources (energy, materials, solvent, etc.), which is detrimental to the environment [1].

Herein we discuss the design and development of a new type of fully integrated continuous process for multiphase oxidations at scale. Inorganic oxidants are generated electrochemically in an aqueous phase from non-hazardous inorganic salts and electricity [2]. The aqueous oxidant solution is subsequently dispensed to mix with reactants in an organic solvent (immiscible) forming a liquid/liquid reactive flow. An unstable emulsion is generated from the reactive flow using either a surface membrane module or a high shear mixer in a recirculation loop. The unstable emulsion is fed forward in to a continuously pulsed flow system as a way of overcoming mass transport limitations by enhancing liquid/liquid interactions [3] and maintaining the emulsion in a kinetically dispersed state. After an appropriate residence time the emulsion is eluted into a coalescence column allowing for a facile separation of the two phases. The aqueous phase is retained and recycled back to the electrochemical cell whereas the organic phase is collected for product analysis, simplifying the workup procedure.

The experimental mini-plant is supported by a predictive multiphase model that has been developed to incorporate different time constants (residence time, droplet formation and coalescence rates as well as intrinsic reaction rate) in order to identify appropriate operating regimes for any given oxidation process.

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VIRTUAL PRESENTATIONS

ELECTROMAGNETIC CATALYTIC REACTOR OF WATER TREATING FROM OILS AND HYDROCARBONS

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The problem of clearing of water resources from oil pollution is rather actual now. Annual total emission of mineral oil in the seas and oceans as a result of consequences of extraction and emergencies is estimated on different sources, including the National academy of sciences the USA on the average from 6 up to 8 million tons. Nevertheless, the problem of operative and effective liquidation of consequences of similar emissions is far from the decision in view of low efficiency of existing technological decisions, and including, absence high-efficiency the reactor equipment. The majority of known processes of clearing of water environments from oil pollution is based on use the methods of oxidation [1], flotation [2], absorbtion [3], and also methods of biological clearing [4]. Under the total characteristics, including productivity, a degree of clearing, simplicity of technological decisions, the economic and power efficiency, the mentioned ways are conditionally suitable for the decision of similar problems.

The clearing process of water environments from oil pollution and dangerous hydrocarbons aromatic and olefinic the lines, based on use is developed and tested in industrial scale as basic reactionary unit of the device of electromagnetic processing water environments. The principle of work is based on the phenomenon of acceleration microparticles association of mineral oil in conditions of interaction of an external variable magnetic field with ferromagnetic sorbent which particles have own constant magnetic field. As a result of such interaction there are intensive association processes the hydrocarbonic components being consequence of concentration in places of impacts of ferromagnetic particles of electromagnetic, thermal and mechanical energies. Further, passing through the polysorbtional layers, the integrated particles of hydrocarbons are absorbed much faster, than similar particles of smaller diameter.

Working parameters of a reactor electromagnetic association:

Initial concentration of mineral oil – 100 ÷ 1 mg/L

Final concentration of mineral oil – 0,5 ÷ 0,05 mg/L

Working volume of a reactor – 30 L

Productivity on initial water – Up to 100 m^3/h

Operating mode – Continuous

Working temperature – 0 ÷ 50 °C

Working pressure – 0 ÷ 1,0 MPa

Besides direct use of the specified installation during water treating, there are variants of her modification, allowing her use in a number of adjacent tasks of oil extracting and processing. In particular, her use is planned during preliminary processing, tars, bitumen sand, in manufacture of dyes, etc. spheres.

The general distinctive characteristics of installation:

1). High efficiency;
2). Stability to a high level of pollution of communications (a rust, sand, fine stones);
3). Standardization of a design with an opportunity of fast replacement of elements (a grid, a pipe, nozzles and so forth);
4). Absence of a problem of deterioration in case of use the plastic case of a reactor.

Installation has passed industrial tests in a zone of the Caspian pool: Russia, Republic Dagestan.

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THE KINETICS AND MECHANISM OF LOW-TEMPERATURE CARBON MONOXIDE OXIDATION BY MOLECULAR OXYGEN ON $PdCl_2$-$CuCl_2/\gamma$-Al_2O_3 CATALYTIC SYSTEM

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The reaction of low-temperature oxidation of carbon monoxide by oxygen is of fundamental scientific interest, since it is one of the simplest oxidation reactions and can be used to identify general features of processes with molecular oxygen participation.

Among the low-temperature catalysts used for the reaction supported metal-complex catalysts are the least studied. Palladium-copper-based catalysts are the most promising of this group [1-3]. This report deals with new data about kinetics and mechanism of low-temperature carbon monoxide oxidation by molecular oxygen on $PdCl_2$-$CuCl_2/\gamma$-Al_2O_3 catalyst.

Previously, study of the active components state on the surface of the $PdCl_2$-$CuCl_2/\gamma$-Al_2O_3 catalyst was conducted by X-ray absorption spectroscopy (XAS), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and diffuse reflectance IR Fourier transform spectroscopy (DRIFTS) and preliminary kinetic investigation was carried out [3,4].

The kinetics regularities were obtained by the method of single-factor experiment. The advancing of hypotheses about the mechanism was carried out on the basis of information of the state of palladium and copper on the surface of alumina during the process. Discrimination of hypothical mechanisms of the reaction was carried out on the basis of known physico-chemical data [4] and on the results of kinetic experiments. Adequate structural kinetic model of the low-temperature oxidation of carbon monoxide is developed. This model describes the dependences of the rate of CO_2 formation as function of the partial pressures of the reactants in a wide range of its variation. It has been shown that the most probable mechanism of the reaction under conciderature includes carbon dioxide formation by interacting the surface complexes of Pd(I) and Pd(II), coordinating carbon monoxide and water, with surface complexes Cu(I), coordinating molecular oxygen.

The best variant of the mechanism can be represented by the following scheme:

$$X_2Pd_2(I) + CO \xrightleftharpoons{K_1} X_2Pd_2(I)(CO),$$

$$X_2Pd_2(I)(CO) + CO \xrightleftharpoons{K_2} X_2Pd_2(I)(CO)_2,$$

$$X_2Cu(I)_2 + O_2 \xrightleftharpoons{K_3} X_2Cu(I)_2(O_2),$$

$$X_2Cu(I)_2(O_2) + CO \xrightleftharpoons{K_4} X_2Cu(I)_2(O_2)(CO),$$

$$X_2Pd_2(I)(CO) + 3H_2O \xrightleftharpoons{K_5} [X_2Pd_2(I)(COOH)]^- H_3O^+ (H_2O),$$

$$[X_2Pd_2(I)(COOH)]^- H_3O^+ (H_2O) + X_2Cu(I)_2(O_2) \xrightarrow{k_6}$$

$$\xrightarrow{k_6} [X_2Pd_2(I)(OOH)]^- H_3O^+ + CO_2 + X_2Cu(I)_2 + H_2O,$$

$$[X_2Pd_2(I)(OOH)]^- H_3O^+ + CO \xrightarrow{k_7} X_2Pd_2(I) + H_2O_2 + H_2O,$$

$$2H_2O_2 \rightarrow 2H_2O + O_2.$$

Fig. 1. Scheme of mechanism

$$r = \frac{k_1^a \cdot P_{CO} \cdot P_{H_2O}^3 \cdot P_{O_2}}{d}$$

$$d = 1 + k_2^a \cdot P_{O_2} + k_3^a \cdot P_{O_2} \cdot P_{CO} + k_4^a \cdot P_{CO} +$$
$$+ k_5^a \cdot P_{CO}^2 \cdot P_{O_2} + k_6^a \cdot P_{CO}^2 + k_7^a \cdot P_{CO}^3 \cdot P_{O_2} +$$
$$+ k_8^a \cdot P_{CO} \cdot P_{H_2O}^3 + k_9^a \cdot P_{CO} \cdot P_{H_2O}^3 \cdot P_{O_2} +$$
$$+ k_{10}^a \cdot P_{CO}^2 \cdot P_{H_2O}^3 \cdot P_{O_2} + k_{11}^a \cdot P_{H_2O}^3 \cdot P_{O_2}$$

Fig. 2. Equation

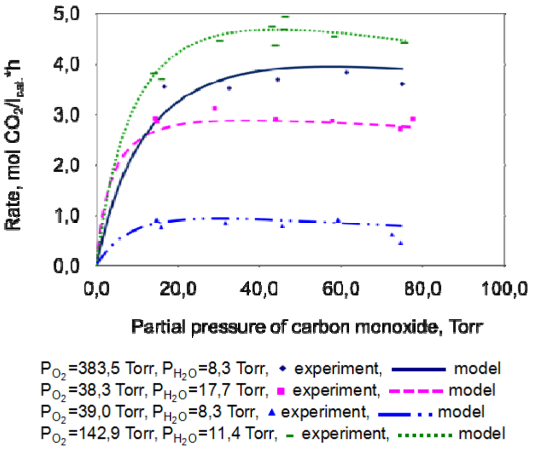

Fig. 3. Carbon dioxide formation rate as a function of carbon monoxide partial pressure

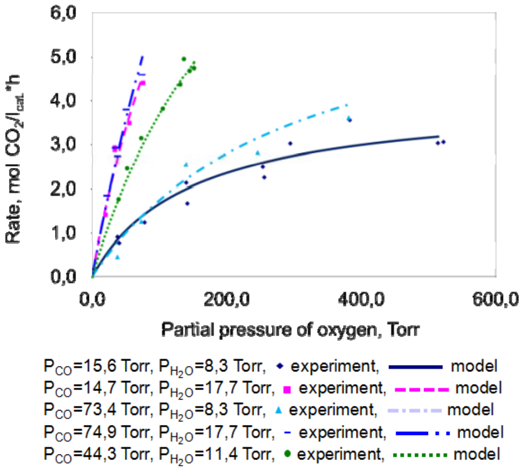

Fig. 4. Carbon dioxide formation rate as a function of oxygen partial pressure

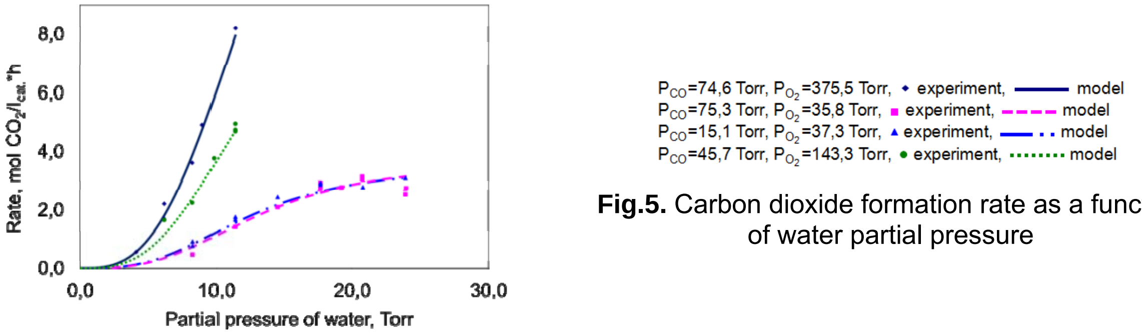

Fig.5. Carbon dioxide formation rate as a function of water partial pressure

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ULTRA-DISPERSED IRON POWDERS AS CATALYSTS OF LIQUID HYDROCARBONS SYNTHESIS BY FISCHER-TROPSCH METHOD

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Topicality of Fischer-Tropsch process using nowadays is conditioned, first of all, by oil-dissolved gas recycling at mines situated remote from gas-refining factories. High hydrocarbon range synthesis – from methane to heavy paraffins – is possible in dependence of using catalysts and process carrying out conditions. The hydrocarbon gas refining to synthetic liquid hydrocarbons (motor fuels, diesel, paraffins, olefins, etc. used both for on the spot consumption – provision by fuels and oils for motor vehicle transport, diesel-driven generators, etc. – and for shipping to another regions in liquid form) is recognized the most perspective [1].

The aim of this work is studying of catalytic activity of ultra-dispersed iron powders derived by conductor electric explosion method in media of different gases (CO, CO_2, Ar).

The samples of powders were derived at Institute of high technology physics of TPU by methods described in the work [2]. The «SORBI-M» machinery was used for quantifying of powder samples specific surface area. This apparatus uses BET adsorption theory for calculations. Measurement results is shown in table 1.

Table 1. The powders specific surface area

Metal (media)	Fe (Ar)	Fe (CO)	Fe (CO_2)
Surface area, m^2/g	5,627	8,03	8,345

The powders makeup was studied by X-ray phasic analysis method. The analysis was carried out with Shimadzu XRD–7000 S (Japan) diffractometer with independent scanning mode of a sample in range of $\theta - 2\theta$ (Bragg's angle).

During decoding of sciagrams it was identified that the major part of substance is in X-ray amorphous condition. The presence of iron monoxide is detected in the makeup of catalyst derived in media of carbon monoxide. Iron oxide forms during decay of carbon monoxide and due to originated atomic oxygen which easily intrudes to iron crystal latitude. There wasn't observed any amount of iron monoxide in the powder samples derived in media of nitrogen or carbon dioxide. All samples contain different iron crystalline modifications, mostly is α-Fe. Analysis shown that the powders are available for use as catalysts of liquid hydrocarbons from CO and H_2.

Research of derived catalysts was carried out in the catalytic system working under high pressure. A 1-2 mm fraction of catalyst was selected for experiments. Volume of loaded catalyst in each test is about 8 cm^3. Simplified scheme of catalytic system is shown below.

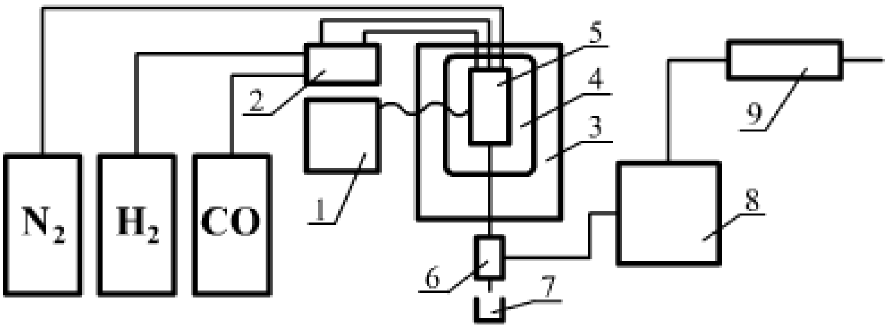

Figure 1. Catalytic system scheme: 1 – control console panel, 2 – digital flowmeter, 3 – heat chamber, 4 – heat jacket, 5 – reactor, 6 – separator, 7 – receiver, 8 – gas chromatograph, 9 – air vent

The catalysts doesn't need pre-reduction in that active surface forms at a stage of electric burst. Total conversion level of carbon monoxide reached about 80 % at T = 280–285 °C. At a further temperature increasing there is no significant conversion level rise, but yield of by-product – carbon dioxide – grows higher. The absolute value of carbon monoxide total conversion level at examined temperatures is high enough that proofs by comparison with different literature data. At lower hydrogen concentration is syngas carbon monoxide conversion level decreases but remains at enough high level. It lets make a conclusion that the catalyst is applicable for synthesis of hydrocarbons from CO and H_2 at low concentration of hydrogen in reactants mixture.

Chromatographic analysis of liquid products synthesized at 290 °C and H_2:CO = 2:1 reactants ratio shown that oxygenates are totally absent that determine low octane number of liquid mixture (about 60 points). There is high enough contain of isoparaffins, low amount of aromatics and olefins in derived products.

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CHEMICAL SYNTHESIS BY MECHANICAL ACTIVATION IN THE VIBRATING MULTIFUNCTIONAL CHEMICAL REACTOR

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At the International Conferences CHEMREACTOR-19, 20, 21 developed in INEOS RAS the vibrating multifunctional reactor, allowing to carry out in a single reaction volume of dissolution processes, synthesis, crystallization, filtration, washing, distillation, conductive drying in a vibrated bed extraction, to obtain crystalline products a predetermined particle size distribution was submitted. Creation of such a reactor, which is provided by intensive mixing of the processed products without the use of mixing devices and seals in the working volume in which the working chamber is autonomous, easily removable and washed, simple geometric shapes without stagnant and difficult to rinse zone, which does not use a gas coolant, and so on provides access to a qualitatively higher level to solve the problem of obtaining and purification of the products of chemical synthesis, allows you to create on the basis of such devices, flexible chemical-technological systems that can quickly and cost-effectively be reconstructed on the new products. The latter is especially important for light-duty and multiproduct manufacturing especially pure chemical substances, synthetic drugs, in particular endocrine and anti-cancer, hormonal [1,2,3,4].

However, for chemical syntheses, initiated by mechanical activation of solid phase products, significant constructive changes in the vibration apparatus be necessary, taking into account specificity the grinding process. The main problems to be solved are as follows:

1. Transfer of solid milled product with the vapors resulting from chemical synthesis during mechanical activation. The filter element of the existing multi-reactor prevents delay dispersion of solid particles less 10-20 mkm. Furthermore, accumulation of unreacted solid particles on the surface of the filter outputs them from chemical process, which reduces its effectiveness.

2. Dosage of the solid phase in the working chamber vibrating at its temperature of 300 °C to ensure the operation of the reactor in the continuous mode.

3. Increase the efficiency of grinding and mechanical activation by creating additional traffic circulation grinding bodies inside the cylindrical working chamber, but close to the vertical oscillations of circular vibration gearing existing apparatus.

The report provides a detailed description of the solution of these tasks and examples of mechanochemical processes in vibratory multifunction reactor.

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THE NANOPOROUS POLYMERIC MEMBRANES FOR THE NEW DESIGN MODULE FOR AMMONIA SEPARATION

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Over the last decades, the considerable focusing on application of polymeric membranes for gases purification and separation was observed due to profitability and environmental friendliness of this method compared to such methods as distillation, crystallization and sorption [1,2]. The primary objective in the development of novel gas separation membranes is to achieve both the high values of permeability and selectivity in one material [3]. One of the promising approaches to achieve the combination of aforementioned properties is a creation of an amphiphilic copolymers, the most prospective ones of which is the organic-inorganic polymers with a block structure [4,5].

The paper presents the results of the study of the gas separation membrane module efficiency, the main part of which is the organic-inorganic polymeric membranes, obtained on the basis of macroinitiator, toluene 2,4-diisocyanate and polyhedral octaglycidylsilsesquioxane (Gl-POSS).

Polymers synthesized without Gl-POSS have the supramolecular structure similar to honeycomb composed of globules of a flexible component and associates of a rigid O-polyisocyanate block. These samples exhibit the high permeability of gases investigated in the present paper and relatively low values of ideal selectivity for separation of ammonia from other gases.

With the Gl-POSS content from 2 to 8 %, at which the frame supramolecular structure with the ordered nanopores arrangement is formed, and also it is observed the maximum permeability of gases and minimum values of ideal selectivity for separation of ammonia from other gases (Table).

At the same time, polymeric membranes had obtained with content of Gl-POSS in a range of 0,5-2 % and 10-15 % are characterized by the high permeability for NH_3

only in comparison with other gases and, consequently, the extremely high values of ideal selectivity for NH_3/gas pairs.

On the basis of obtained results, the two mechanismes of gas transport through the polymeric membrane was suggested, corresponding to three concentration ranges of GI-POSS.

Table. Ideal selectivity for NH_3/gas pairs for the polymeric membranes, obtained with different contents of GI-POSS

GI-POSS, %	α								
	p_1 = 2 bar			**p_1 = 3 bar**			**p_1 = 2 bar**		
	NH_3/He	**NH_3/N_2**	**NH_3/Ar**	**NH_3/He**	**NH_3/N_2**	**NH_3/Ar**	**NH_3/He**	**NH_3/N_2**	**NH_3/Ar**
0.0	1,8	2	1,9	2,7	3,7	3,2	1,98	2,3	2,11
0.1	0,8	2,7	3,4	11	2,8	3,0	2,3	3,19	3,59
0.5	11915	11915	11915	22506	22506	22506	8365	8365	8365
2.0	2	2,7	-	3	3,8	-	2,1	3,1	-
5.0	0,64	1,1	-	1,2	1,7	-	1	1,4	-
8.0	0,27	1,8	1,3	0.3	1,16	1,4	0,4	1,2	1,6
10.0	11,0	14,9	17,5	16.5	27,6	30,6	15,3	22,5	24,9
15.0	7436	7436	7436	6148	6148	6148	7819	7819	7819

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THE INVERSE PROBLEM SOLUTION FOR CATALYTIC REACTIONS

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The determination of kinetic parameters of reactions is considered to be the complex task of chemical kinetics [1]. We have developed the method of determination of elemental stages constant rates of catalytic reactions where there is one basic substance. Now we will examine catalytic reaction with the basic $\mathbf{A}_k$ and intermediate X_j substances passing through the stages

$$\sum b_{ik}\,\mathbf{A}_k + \sum a_{ij}\,X_j = \sum a_{-ij}\,X_j + \sum b_{-ik}\,\mathbf{A}_k\ ,\ i=1,\dots,s;\ j=1,\dots,J;\ k=1,\dots,K, \qquad (1)$$

where there is one basic substance that is $b_{\pm ik}$, $a_{\pm ij}$ are stoichiometric coefficients in the stage i, $\sum_j a_{ij}=\sum_j a_{-ij}$. The dynamics of this reaction in the open non-gradient isometric reactor is described by common differential equation with starting conditions $x_j(t_0) = x_j^0$, $A_k(t_0) = A_k^0$:

$$x_j' = \sum(a_{-ij} - a_{ij})(r_i - r_{-i}) \equiv f_j\ , \qquad (2)$$

$$A_k' = \sum(b_{-ik} - b_{ik})(r_i - r_{-i}) + q^0 A^0{}_k - qA_k \equiv g_k\ , \qquad (3)$$

where x_j is the concentration of intermediate substances, $\sum x_j=1$; $r_{\pm i}=k_{\pm i}\prod_j x_j^{a\pm ik}\prod_k A_k^{b\pm ik}$ are the stages' rates in forward and reverse directions (1/c), $k_{\pm i}$ are the constants of stages' rates, q^0, q and $A^0{}_k$, A_k are the feed rates (1/c) and the concentrations (mols and parts) of basic substances at input and output of the reactor. Here are the results of nonstationary experiment with value set concentrations A_{kn} time t_n with the step $h=t_n-t_{n-1}$, where $n=1,2,3,\dots$ is the number of measurement. We will choose necessary number of points for calculations from this set, we will substitute them in (3) and we will obtain a system of equations for the determination 2s of unknown constants of stages' rates $k_{\pm i}$:

$$A_{kn}' = \sum(b_{-ik} - b_{ik})(r_i - r_{-i}) + q^0 A^0{}_{kn} - qA_{kn} \equiv g_{kn}(k_{\pm i},\, x_{jn},\, A_{kn}),\ k=1,\dots,K. \qquad (4)$$

This system of equations includes observable (the concentrations of basic substances A_{kn}), unobservable (the concentrations of intermediates x_{jn} and derivatives from the concentrations of main substances A_{kn}'), features of reactions is solved when the number of equations does not exceed the number of unknown constants $K\le 2s$. We will exclude from the system (4) the concentrations of intermediates with the help of nonstationary kinetic conservation laws that are found out from the equations (2) - (3) with the help of their linear combinations such as

$$x_j' + \sum_k \alpha_{km} A_k' = \sum_k \alpha_{km}(q^0 A^0_k - qA_k),\ j=1,\ldots,J;\ k=1,\ldots,K;\ m=1,2,\ldots,M. \qquad (5)$$

where α_{km} is the combinations of stoichiometric coefficients of the reaction (1), m is the number kinetic conservation laws, M is the number of kinetic conservation laws. Such kinetic conservation laws do not depend on the constants of stages' rates, they are linear in the derivatives x_j' and are closely described by iterative formula obtained by replacing derivatives (5) by finite differences $x_{jn}' \approx (x_{j,n} - x_{j,n-1})/h$:

$$x_j,\ n^* \approx x_j,\ n = x_j,\ n-1 + \sum_k \alpha_{km}\ (q^0 A^0_k - qA_k,\ n-1-A_{kn}')\ h,\ n = 1,2,3,\ \ldots,\ N. \qquad (6)$$

The ratios (6) allow to calculate the approximate concentration of M in intermediates at any time and to exclude them from (5).

We will calculate the approximate rate of change in the concentrations of the main substances to solve the system (4) - (6) and the determination of unknown constants of stages' rates

$$A_{kn}' \approx \nu_{kn} = (A_{kn} - A_{k,n-1})/h, \qquad (7)$$

where A_{kn} и $A_{k,n-1}$ are the concentrations of main substances at this and further periods of times. Following this (2)-(7) shows:

$$\nu_{kn} \approx g_{kn}(k_{\pm i},\ x_{jn}^*,\ A_{kn}),\ k=1,\ldots,K. \qquad (8)$$

These ratios link the constants' rates with the rates of change concentrations in key substances that are calculated by the data of nonstationary experiment for any time *t* by the formula (7). We will choose required number of different time points n=1,2,... in any nonstationary experiment for the calculations and we will measure the relevant concentrations of A_{kn}. Substituting these values in (8) taking into account (6) we will obtain the system of linear equations for determination of unknown constants of stages' rates in the reaction (1). The described method can be applied for the reactions passing through the stages not containing the basic substances. In addition to this the constants of gross-stages' rates obtained by the combination of these stages with the stages where are basic substances are determined. The examples of using the method for two - and three-stage reactions are shown in the report.

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EFFECT OF POWER RADIATION ON THE POLYCONDENSATION OF LACTIC ACID UNDER MICROWAVE SYNTHESIS CONDITIONS

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At present, microwave irradiation (MW) is widely used in the synthesis of biopolymers [1-2]. MW application helps to significantly reduce reaction time and, from the other hand, to increase the yield and product molecular weight. Besides, this kind of synthesis is useful in eco-friendly methods development for the synthesis of biologically active compounds [1, 3]. Reactions under MW conditions are susceptible to energy distribution in the reaction chamber and different speeds occurs in monomode and multimode microwave reactors [1].

Lactic acid oligomer is an important intermediate in the synthesis polylactic acid. Also, it is used for drug delivery in clinical practice [1, 3]. The main disadvantage of the synthesis lactic acid oligomer is a long reaction time. Lactic acid (LA) synthesis was carried out under thermal dehydration conditions more than 6 hours [2].

In this paper we demonstate the influence of microwave power in the process of dehydration/polycondensation of LA in multimode reactor.

LA was charged 20 g in 100 ml flask, placed in a reactor and sparged with nitrogen at a pressure of 200 mm Hg, under radiation power of 80, 130, 280, 360 and 500 watts.

The synthesized samples were investigated by IR and ^{1}H NMR spectroscopic methods. Molecular weight was determined by viscometric method.

On the figure 1 we can see that the LA sample temperature change depending on the time and radiation power under MW conditions. The temperature of LA samples under MW power at 280, 360, 500 W were the same and equal 215°C.

According to the data (Table 1) ^{1}H NMR and IR suggested that the 80 W mostly removed physically bound water molecules. At 130-280 W, water removal and LA polycondensation were carried simultaneous and the conversion of LA changed from 64 to 67 %.

LA polycondensation proceeds most effectively at 360 watts.

Vacuum MW application results the increasing of product molecular weight.

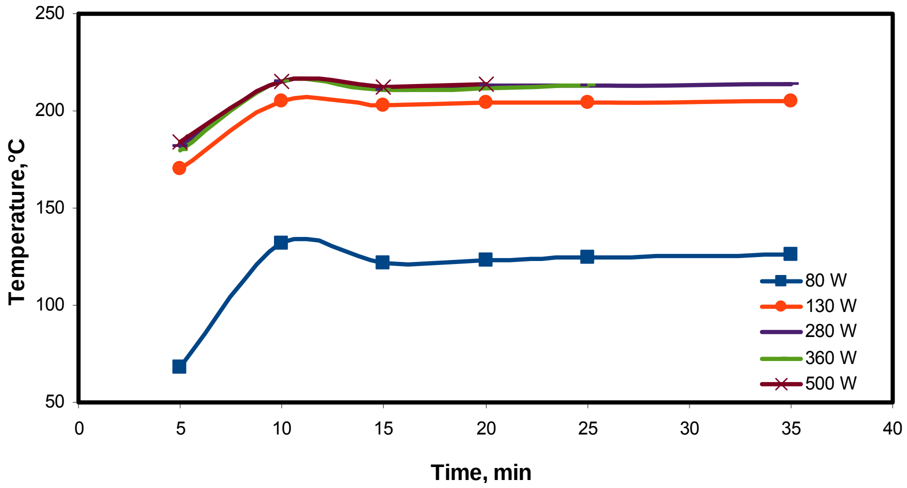

Fig. 1. The dependence of the lactic acid sample temperature from the time under microwave irradiation: 1 - 80 W; 2 - 130 watts; 3 - 280 W; 4 - 360 W; 5 - 500 W

Thus, keeping the LA oligomer under vacuum for 1 hour at 360 W helps to increase the product molecular weight in 10 times.

Table 1. Physical-chemical properties of the LA oligomer

Power (heating time), W(min)	1H NMR chemical shifts the LA oligomer, ppm.				M, [Da]
	δ, m (CH) LA	δ, m (C-H) LA oligomer	δ OH - groups LA	The conversion, %	
80(35)	4,3	5,1	7,3	46	-
130(35)	4,4	5,2	6,5	64	270
280(35)	4,4	5,2	7,0	67	310
360(15)	4,4	5,2	6,8	83	750
500(15)	4,3	5,1	7,5	66	440
280(165)	4,3	5,2	-	95	16350
360(60)	4,3	5,2	8,2	94	9350

From the obtained data it ensue that the process of LA polycondensation at the same temperature (215 °C) is determined by power radiation of MW: under radiation power of 360 W the process of dehydratation/polycondensation was carried out faster, than at 280 W, i.e. there is a so-called "microwave effect".

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CONVERSION OF ETHANOL INTO BUTADIENE-1,3 IN THE PRESENCE OF AN INITIATOR

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It is known that ethanol is prepared in a variety of ways, from petroleum feedstock, from the green mass. Today the focus is on ethanol produced from the non-food green mass.

Ethanol can serve as raw material for rubber, motor fuels, polyethylene and many other valuable products of the petrochemical industry.

The process for preparing butadiene-1,3 known as the Lebedev process today is again of great interest in connection with the problems of resource-saving. However, the selectivity of the process is 44 % and it shows the importance of finding the ways to intensify the process. Laboratory of chemistry and petrochemical synthesis (TIPS RAS) provides an alternative catalyst (ZAK-16), which together with the initiator, increases the selectivity by 3,2 % and the reaction cycle to 180 h. [1].

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PROCESS PARAMETERS' INFLUENCE ON EFFICIENCY OF ALKYLATE COMPOSITION AND OCTANE NUMBER

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Environmental requirements stricter for commodity gasoline leads to an inevitable increase in demand for alkylate, which is the product of the isobutene alkylation with olefins, and makes it an ideal component of motor fuel. For example, according to the EIA (Energy Information Administration of the USA) in the near future alkylates will be 20-25 % of the total gasoline in the United States [1].

Operation efficiency increasing for alkylation process is a very relevant and important task in terms of improving energy and resource efficiency of its work. To achieve this it is necessary to develop and introduce new technologies in the industry, catalysts, reactor unit.

Mathematical modeling is a useful tool for selecting the most effective ways to optimize the industrial alkylation units.

The study aim is investigating of feed composition influence on the alkylate quality using the developed mathematical model of isobutane sulfuric acid alkylation with olefins [2].

Feedstock impurities in alkylation process include normal paraffin hydrocarbons with low reactivity (propane, n-butane, n-pentane), which was diluted with a hydrocarbon phase and, therefore, reduce the concentration of isobutane and butylenes therein.

The calculations based on model showed that the concentration of propane and n-butane does not influence on alkylate research octane number, but increases its output in the material balance. This is due to the fact that propane and n-butane being ballasted are not involved in the alkylation reaction. Once the content of these components increase the alkylate yield is reduced (see Table 1).

Table 1 – Propane and n-butane content influence on alkylate yield

Component content in feed, % mas.	Alkylate yield, kg/h
Propane content in combined feed, % mas.	
1,00	13174
2,00	12908
3,00	12643
n-butane content in combined feed, % mas.	
11,0	12890
11,5	12781
12,0	12624

Studies have shown that increasing the content of propylene decreases alkylate research octane number (Table. 2).

Table 2 – Propylene content influence on octane number

Propylene content in combined feed, % mas.	Alkylate research octane number
0,03	95,74
0,10	95,53
0,30	95,07

Propylene is reacted with isobutane to form 2,4-dimethylpentane, 2,3-dimethylpentane and 2,2-dimethylpentane, which have lower octane numbers.

Calculations have shown that the presence of n-pentane in the feed is undesirable because it affects the quality of the alkylbenzene. High content of ΣC_5 and ΣC_{5+} also makes a negative contribution to the properties of the product (Table 3). Analysing industrial plant operation data, one can conclude that the content of components C_5 and C_{5+} varies slightly. Within these concentrations range effect on alkylate RON is insignificant.

Table 3 – C_5 and C_{5+} influence on alkylate octane number

Component content in feed, % mas.	Alkylate research octane number
C_5 content in combined feed, % mas.	
0	95,76
0,22	95,74
0,40	95,72
C_{5+} content in combined feed, % mas.	
0	95,74
0,05	95,50
0,10	95,27

Thus, the applied use of mathematical models allows predicting the effect of impurities in the composition for alkylate octane. Calculations have shown that increasing the propylene content in the feed at 0.3 % octane decreases alkylate by 0.5-1.0 points. Propane and butane are not significantly affect the octane number of the product, but at the same time increasing their content in the feed leads to a decrease in the yield of alkylate. Components and ΣC_5 ΣC_{5+} does not have a significant impact on the quality of alkylate.

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VP-10

COMPUTATIONAL CHEMISTRY AS A TOOL FOR STUDYING OF THE PROCESSES IN THE CHEMICAL REACTORS ON THE MOLECULAR STAGES LEVEL

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Although computational chemists frequently develop and refine software tools, their primary interest is in applying software tools to enhance chemical knowledge. The challenges for computational chemistry are to characterize and predict the structure and stability of chemical systems, to estimate energy difference between different states, and to explain reaction pathways and mechanisms at the atomic level. Meeting these challenges could eliminate time-consuming experiments. Software tools for computational chemistry are often based on empirical information. To use these tools, you need to understand how the technique is implemented and the nature of the database used to parameterize the method.

A number of useful concepts have been introduced to describe the electronic structure, the interaction energies and the dynamics of adsorbents on surfaces. It is now possible to describe at a semi-quantitative level the electronic structure and energetic of adsorption on metal surfaces. The accuracy is still not sufficient to calculate rates of chemical reactions, but it is sufficient for a semi-quantitative description of adsorption and reaction processes, and in particular for comparing different systems. The latter is particularly important if one wants theoretical input into a search for surfaces with a desired activity or selectivity for a given chemical reaction. Even if we are at a point where bond energies and activation energies can be calculated for the simplest systems with a reasonable accuracy, there is a strong need for models and simplified theories of binding. The large scale calculations can be viewed as computer experiments and just as for real experiments we need a conception framework for an understanding or rationalization of the results. If we are for instance interested in finding new alloy surfaces with a particular reactivity or bond strength towards a certain molecule it would be extremely helpful with an understanding of the most important factors determining the ability of a surface to bind or react with the molecule in question.

What determines the catalytic activity of a given surface for a given chemical reaction? One of the aspects about solid surfaces that have the largest fundamental and technical importance is the way in which chemical reactions are affected by the presence of a surface. Many catalytic reactions are structure sensitive, meaning that the rate depends on the geometrical structure of the surface. Almost all of them proceed with rates that are much larger at a surface than in the gas or liquid phase. For reactions with more than one possible product the presence of a surface can change the selectivity [1]. On the other side, the poisoning and promoting effect that co-adsorbates can have on the rate of a reaction for a fixed surface structure of the catalyst is ascribed to an electronic factor [2]. These principles are used extensively in all industrial production of chemicals.

Our research effort is aimed to make accurate predictive chemical kinetics of elementary stages in the chemical reactor; this is a challenging goal which necessarily includes a range of science advances. Our research spans a wide range from quantum chemical calculations on individual molecules and elementary-step reactions, through the development of improved rate/thermo calculation procedures, the creation of algorithms and software for constructing and solving kinetic simulations, the invention of methods for model-reduction while maintaining error control, and finally comparisons with experiment.

There are attempts to model at a realistic level, both structural and energetic aspects of the elementary steps of chemical reactions in this paper. Such models must of necessity include quantum chemical descriptions of bond breakage and formation one and also quantum-mechanical description of researched molecules directly involved in the elementary steps of reaction.

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VP-11

OUTPUT MULTIPLICITY ANALYSIS OF METHYL TERT-BUTYL ETHER REACTIVE DISTILLATION SYNTHESIS

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Nowadays, reactive distillation (RD), which includes combined reaction and separation process in one unit operation, is considered by industries as object of interest. Due to its thermodynamic and economic advantages, RD can be discussed as a successful example of the process intensification [1]. On the other hand, the combination of chemical reaction and separation in a single column reduces the number of valves available for control and causes high non-linearity, which can lead to steady-state multiplicities [2]. For example, output multiplicity, with multiple output values for the same input parameters, causes the column to drift to an undesirable steady-state [2].

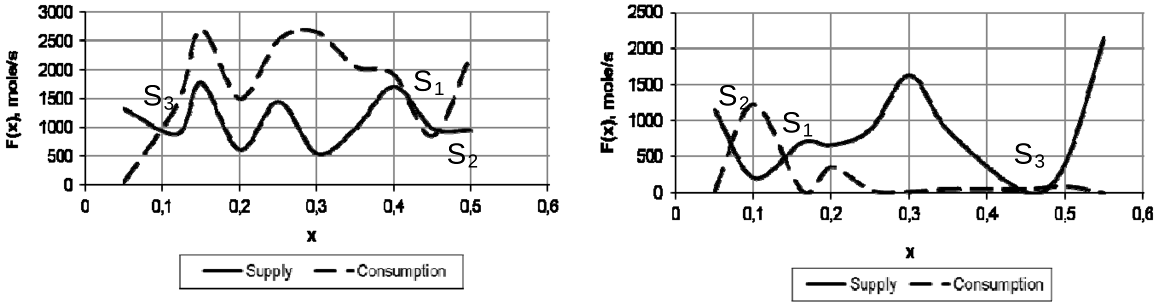
The aim of the work is to present output multiplicity analysis of RD process based on the previously developed mathematical model of methyl tert-butyl ether (MTBE) synthesis [3].

Material balance equation of the reactive section of the column can be represented as functions of substance consumption and supply

$$\begin{cases} F^{\sup ply} = \dfrac{L_d}{R} + \dfrac{L_d}{R} \cdot \dfrac{L_d}{\cdot k_i} + \left[\dfrac{L_d}{R}\right] \cdot \dfrac{{L_d}^2}{k_i \cdot k_{i-1}} + \ldots + \dfrac{{L_d}^i}{\prod\limits_{i=1}^{M} k_i} + k_f \dfrac{x^{i-but} \cdot \gamma^{i-but}}{x^{MeOH} \cdot \gamma^{MeOH}} \\ F^{consumption} = L_d \dfrac{x_i}{x_d} + k_f \dfrac{x^{MTBE} \cdot \gamma^{MTBE}}{K_{eq}\left(x^{MeOH} \cdot \gamma^{MeOH}\right)^2} \end{cases}, \quad i=1,2\ldots s \qquad (1)$$

L_d – distillate flow rate, mole/s; s – number of stages in reactive section; k_i – vapor-liquid equilibrium constant; k_f – forward reaction rate constant; K_{eq} – equilibrium constant; R – molar reflux ratio; γ – activity coefficient; x – liquid molar part; superscripts *i-but*, *MeOH*, *MTBE* correspond to isobutylene, methanol and MTBE respectively.

Figure 1 shows relationships between functions F^{supply}, $F^{consumption}$ and component concentration.



a) *b)*

Figure 1. Dependence of F^{supply} and $F^{consumption}$ from concentration of components in reactive section of the column
a) Methanol concentration, b) MTBE concentration.

According to fig. 1-2, the points of intersection of supply and consumption lines are related to output steady states of reactive section of the column. Steady states compositions are presented in Table 1.

Table 1. Material flows compositions of output steady states in reactive section

S_1		S_2		S_3	
$x^{i\text{-}but}$	0.08	$x^{i\text{-}but}$	0.08	$x^{i\text{-}but}$	0.01
x^{MeOH}	0.41	x^{MeOH}	0.47	x^{MeOH}	0.11
x^{MTBE}	0.14	x^{MTBE}	0.08	x^{MTBE}	0.47
$x^{n\text{-}but}$	0.37	$x^{n\text{-}but}$	0.37	$x^{n\text{-}but}$	0.41
X, %	28.9	X, %	16.5	X, %	97.0

Here Table 1 illustrates that the most desirable steady state is S_3, which corresponds to the best product yield (X).

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VP-12

ANALYSIS OF THE DEACTIVATION OF SULFURIC ACID DURING THE ALKYLATION OF ISOBUTANE WITH BUTENES

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Alkylation catalyst options for refiners today consist of hydrofluoric (HF) and sulfuric (H_2S0_4) acids. These acids increase not only the rate of primary reactions but also the rate of secondary reactions, such as polymerization, disproportionation, cracking. Some secondary reaction products tend to lower the octane and will be retained in the acid phase, ultimately becoming the acid soluble oils responsible for acid consumption.

The aim of this work was to study sulfuric acid deactivation during the alkylation of isobutane with butenes with the mathematical model.

The concentration of isobutane in the reaction zone is the important operating variable that impacts the product quality. Using the mathematical model of isobutane alkylation with olefins [1] it has been found that high concentration of isobutene in the reaction zone decreases the likelihood of olefin-olefin polymerization that will result in low concentration of acid soluble oils (ASO) in the sulfuric acid (Fig. 1).

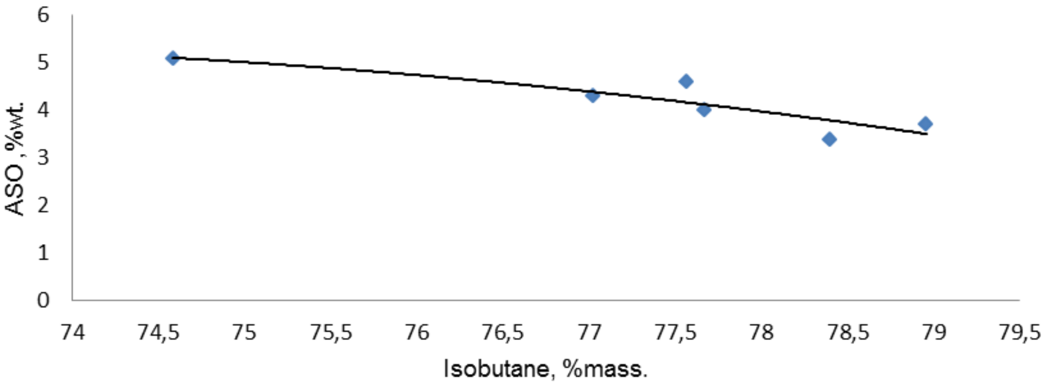

Fig. 1. Dependence of the concentration of the ASO on the concentration of the isobutane in the reactor (model)

It was experimentally proved that the values of optimal residence time of the hydrocarbon in the reactor most often range from 20-30 min although they can be higher or lower. Higher residence times tend to increase sulfuric acid consumption rates and concentration of the ASO in the sulfuric acid (Fig. 2).

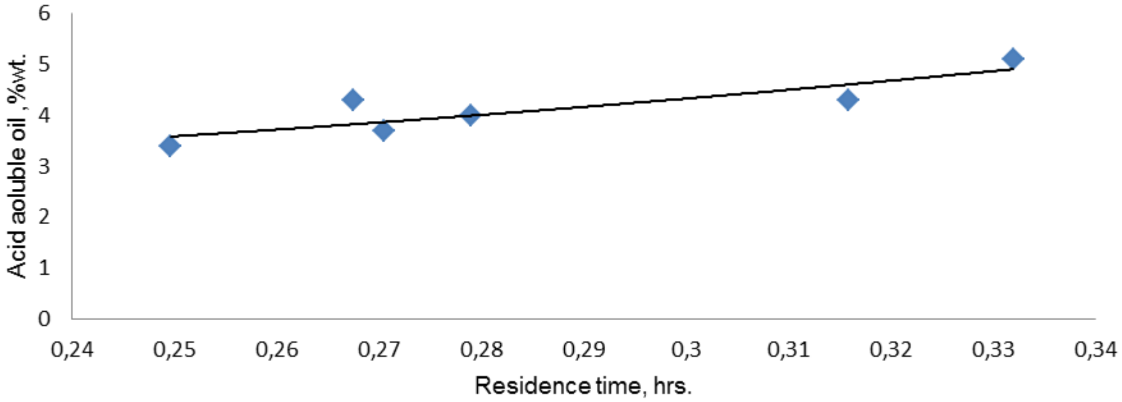

Fig. 2. Dependence of the concentration of the ASO on the residence time (model)

The sulfuric acid catalyst is diluted with acid soluble hydrocarbons and water from the hydrocarbon stream. ASO are formed as by-products in the isobutane alkylation with butene [2].

Using the Semi-empirical method based on NDDO (Neglecting of Diatomic Overlap) approximation at PM3 level in the computational chemistry software Gaussian, kinetic parameters of possible mechanism of ASO formation were calculated (table 1):

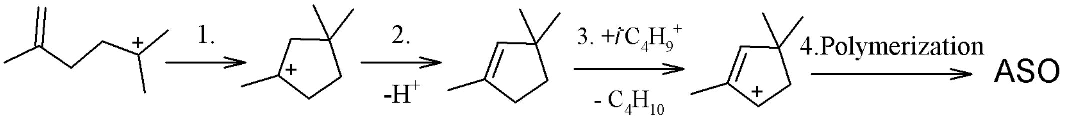

Table 1. The calculated pre-exponential terms in the Arrhenius equation of reaction stages of ASO formation (T = 283 K and P = 4 atm)

Stage	The pre-exponential term, A_0 in the Arrhenius equation
1	$1{,}82\cdot10^{10}$ sec^{-1}
2	$2{,}9\cdot10^{10}$ sec^{-1}
3	5,9·1010 $l\cdot mole^{-1}sec^{-1}$
4	$2{,}5\cdot10^{10}$ $l\cdot mole^{-1}sec^{-1}$

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IMPROVING THE EFFICIENCY OF TECHNOLOGICAL GAS LOW-TEMPERATURE SEPARATION UNIT DEVICES USING SIMULATION DYNAMIC MODEL

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The huge natural gas resources allow considering it as the main primary source of energy and chemical raw materials in the XXI century. This explains the considerable interest to the whole complex of issues related to natural gas resources, its production, transportation and processing. Currently, in technology field of hydrocarbon gases treatment a low-temperature separation process has proven itself. It is based on extraction of liquid hydrocarbons from gas by a single condensing at low temperatures of -10 to -25 °C with gas-chemical division of equilibrium gas and liquid phases and is characterized by low capital investment and operating costs with maximum differential pressure.

Using computer modeling systems based on mathematical models of stationary, does not allow identify and evaluate non-obvious changes in parameters of the devices as a result of inertia of transients occurring in conjugate elements of chemical-technological system [1].

Therefore, work on the construction of mathematical apparatus suitable for the optimization of existing plant and gas field treatment apparatus, included in it, under dynamic conditions is important.

The aim is the development and use of dynamic simulation model of a low-temperature gas separation to predict the performance of devices existing process plant.

This model can be widely used in carrying out of researches of efficiency and safety of units within HAZOP / HAZID methodologies [2].

The results of numerical studies have shown that switching mode in the apparatus for a short time there is the inertia of the system. Thus, in the first separator after switching valve, the number of incoming raw materials continued to decline and then there is a sharp increase in the receipt of raw materials [3–5].

Figure 1 shows that the transition from the initial state (the segment OA) consumption changes does not affect the temperature and pressure in the apparatus (the principle of inertia). Further, with a gradual increase in consumption pressure drop and temperature (segment AB) is observed. When returning a system there is an inverse relationship (cut CO). In the moment of perturbation creation the pressure and temperature also remain constant (segment BC).

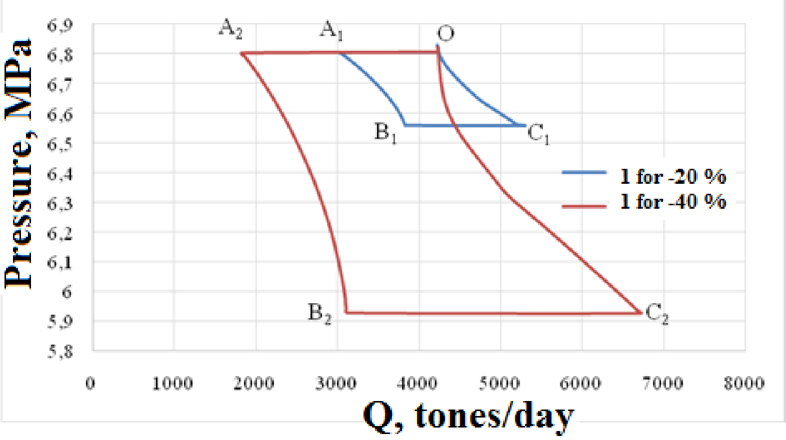

Figure 1. Dependence of pressure in the second separator on the amount of incoming raw materials in the first switching valve

Thus, mathematical model of low-temperature gas separation able to predict the performance of devices existing process plant was developed.

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THE HYDROCARBOXYLATION OF ALKENES COUPLED WITH CARBON MONOOXIDE OXIDATION IN THE SYSTEM $PdBr_2$-$CuBr_2$-TETRAHYDROFURAN-H_2O

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A coupled process with chemical induction can be organized to obtain the desired products from accessible reactants under mild conditions. For this, it is necessary to find a basic reaction that has no thermodynamic and kinetic limitations in the range of conditions used and can be a source of the key intermediate (or catalyst) of the reaction that gives the desired product [1–3].

One of the most frequently used basic reactions is the oxidation of CO into CO_2 (I). This reaction can be a source of various intermediates involved in reactions of different types.

$CO + 0.5O_2 = CO_2$ (I)

The oxidation of carbon monoxide (I) coupled with carboxylation of alkenes into carboxylic acids (II) proceeds in the $PdBr_2$-$CuBr_2$-THF-H_2O system at 30 °C and atmospheric pressure of a mixture of oxygen and carbon monoxide [4, 5].

$RCH{=}CH_2 + CO + H_2O = RCH(COOH)CH_3 + RCH_2CH_2COOH$ (II)

The state and equilibrium of palladium and copper complexes in $PdBr_2$-$CuBr_2$-THF-H_2O system were investigated. The model solutions containing components of catalytic systems in various combinations, as well as the catalytic solutions during the coupled process were studied by UV and Vis-, and IR-spectroscopy. A mathematical treatment of the electronic spectra for model systems $CuBr_2$-LiBr-THF, $PdBr_2$-LiBr-THF was carried out. The equilibrium constants for stages of complex formation and the extinction coefficients of complexes were calculated. The assignment of the absorption bands to different palladium and copper complexes has been carried out.

It was shown that the copper(I) complexes were formed as result of the reduction of copper(II) complexes by carbon monoxide when the $CuBr_2$-THF-H_2O system was purged by CO.

The state of complexes in $PdBr_2$-LiBr-THF system has been studied after purging by carbon monoxide. It has been shown that the palladium(II) carbonyl complexes dominate in $PdBr_2$-LiBr-THF system under carbon monoxide atmosphere (the band at 2104 cm^{-1}).

It has been established that $PdBr_2$, $PdBr^+$, $CuBr_2$ - are dominating complexes in initial catalytic system $PdBr_2$-$CuBr_2$-THF.

Copper exists mainly in the form of copper (I) compounds under the conditions of the conjugated process of alkene hydrocarboxylation. Carbonyl complexes of copper haven't been registered. Palladium is present in the form of a carbonyl complex of palladium (II) and perhaps oxygen and (or) alkene includes in the coordination sphere of palladium.

The possibility of carrying out of allyl alcohol carbonylation process coupled with the oxidation of carbon monoxide (I) was shown. The main product of this process is 2-methyl-3-hydroxypropanoic acid. Kinetic regularities of this process will be studied.

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VP-15

PROSPECTIVE FERRITE CATALYSTS FOR FLUE GASES CLEANING FROM CARBON MONOXIDE

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Exhaust gases of various composition and origin remain serious ecological threat because some traditional components, such as carbon monoxide (CO), keep activity and toxicity against traditional combustion processes as well as catalytic conversion. Under certain conditions, exhaust gases may consist of up to 50 components, which percentage may vary, many of them require different approach to conversion and detoxication. CO is known poison to living beings, it has compact molecule of linear geometry, possess high reaction activity and high penetrating power, so is objectively hard to bound.

Looking across the market, we have to mention efficient commercial catalysts with active phase containing either platinum group-metals (PGM) or rare-earth metals. Despite of varying design and composition, both contain active monophase or a mechanical mix of active phases, both have limited resource, are aware of catalytic poisons and drastic changes in temperature, humidity and exhaust composition. Moreover, such catalysts are rather expensive, and have known problems with utilization of catalyst or regeneration of valuable metals from within the carrier.

Preliminary studies make us believe that specially treated complex oxides of transient metals have structural premises for catalytic activity against exhausts, including but not limited to CO, comparable to those of PGM and ceria, latter well-known in automotive catalysis. These complex oxides may prove valuable in catalysis because they are cheap, stable and immune both to catalytic poisons and operating conditions change. We also believe that solid solutions may increase catalyst lifecycle and activity, comparing to mechanical mix of active phases, traditional to most catalysts present on the market.

In order to design multi-functional catalyst, based on those transient metal oxides, we performed an excessive SEM and XRD study to describe possible phase and structural changes that samples undergo, paying special attention to the way an investigator may control and maintain those changes.

Both metals and oxides of high purity and dispersity are often synthesized by means of thermolysis, corresponding organic salts are decomposed in vacuum or inert atmosphere. According to XRD, double or more complex oxides are formed almost simultaneously with simple ones, forming a solid solution. Unstable equilibrium between individual phases and solid solution is observed for some time under certain conditions, then it spontaneously shifts, so solid solution decomposes to simple oxides. Aiming on complex oxides formation, we performed thermolysis within reduction atmosphere, that let us keeping the equilibrium and preventing complex oxides from decomposition. We used oxalates of corresponding metals for thermolysis mixed with flux, containing various organic ammonia salts, including oxalate, in order to maintain atmosphere control.

Transient metal oxides may continuously form and rearrange structural defects within spinel-like (AB_2O_4) or perovskite-like (ABO_3) structure, that is also valuable for a catalyst, assuming structural stability and self-regeneration possibility. The most promising results were achieved while investigating complex iron oxides (ferrites), structural modification took up to 30% locations of iron oxide, we used Co, Ce, Cu, La, Mn, Ni, Zn oxides as modificators. Fine crystalline mixture of iron oxalate and modifying metal (s) oxalate(s) mixed 4:1 wt, flux amount and composition varied. Calcination time varied from 1 to 24 hours and temperature varied from 200 to 1250 °C. After calcination, the samples were cooled down in the oven for 1 hour and then in a desiccator with a mixture of silica and zeolite filled with high purity nitrogen or argon, where they were naturally cooled down to room temperature. Cooled samples have a regular dispersity of 50-200 nm and are ready-to-use, no need in mechanoactivation or other special measures. Samples were tested for running the catalytic conversion of CO in a flow reactor, or were dispersed into 120 micron particles for the above-mentioned analytical equipment. Analysis of the diffraction data and microscopy allowed to recommend calcination at 900 °C for 3 hours, resulting in optimal composition of active phases – ferrite $MeFe_2O_4$ and magnetite Fe_3O_4, the whole process is well-described by the modified Wagner model.

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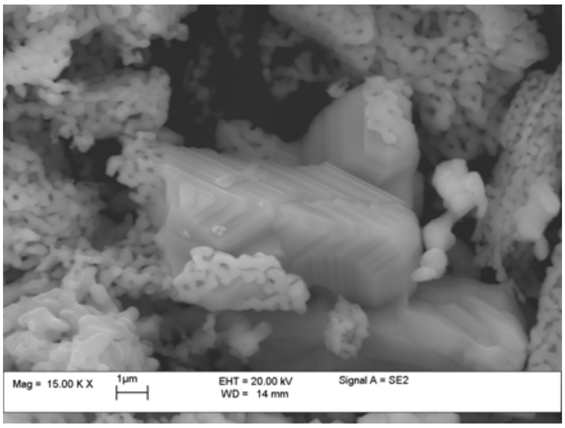

Figure 1. Particle sample – dendrite and spinel sites. SEM.

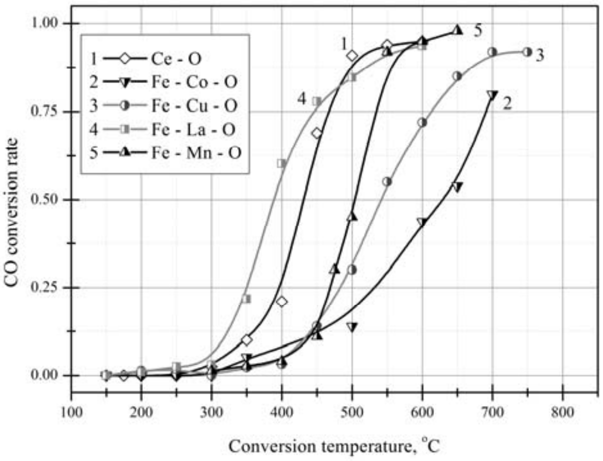

Figure 2. Sample conversion curves

According to SEM and XRD studies, samples contain dendrite-like solid solution of magnetite in magghemite (γ-Fe_2O_3) with local ferrite spinel sites. Both aggregate types (Fig. 1) appear withing the first hour of the calcination process, their composition is also confirmed by elemental analysis. The use of more complex fluxes allowed the authors to control growth and to improve the structure of the product, so that self-arrangement took place, and the target system behaved like an inorganic foam polymer (pore size - 200 nm or less) and looked like HPCM. After 2 more hours of calcination, ferrite grains started to form and local planes began to sprout in one or two directions.

To test conversion productivity the reactor was purged with mixture of carbon monoxide, carbon dioxide and humidified air to simulate the composition and conditions of the flue gases of various origin, including catalytic cracking, CO contents varied 5-20 %, gas temperature was 25 °C and above. All samples performed well, complete CO conversion occured at 600 °C as gaseous mix flow rate was 1 m^3 per hour. According to Fig. 2, catalysts show conversion rate, comparable to both ceria-containing and Pt-containing catalysts, some even overcoming them, like Fe-Mn-O system. To ensure catalyst stability, we performed rigorous testing with rapid temperature and composition change, catalysts performed well, according to SEM and XRD, structural and phase shifts took place when needed, resulting in real-time self-regeneration as expected.

APPLICATION OF INDUSTRIAL DATA OF LG-24/7 IN MODEL OF SULFUR COMPOUND KINETICS IN THE HYDROTREATING PROCESS

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All petroleum fractions are hydrotreated to reduce the content of sulfur compounds in gasoline and diesel fuels. Concomitant effect of this process is the saturation of unsaturated hydrocarbons, reduction of tar containment, oxygenation and slight hydrocracking of hydrocarbon molecules. Hydrotreating is a large-capacity refining process and is used in almost all refineries. The main purpose of this study is to model the kinetics and calculate the mass balance of diesel fuel hydrotreating process including the dynamics of sulfur-containing compounds (SCC), such as sulfides, benzothiophene and dibenzothiophene.

A list of possible chemical reactions has been compiled based on the experimental data [1]. Change of Gibbs Energy of represented reactions has been calculated using HyperChem and Gaussian 09 software packages. Gibbs energies of the reactions are in strong correlation with rate constants of the hydrodesulfurization reactions which have been determined in previous works [2]. Developed kinetic model is presented on the Fig. 1.

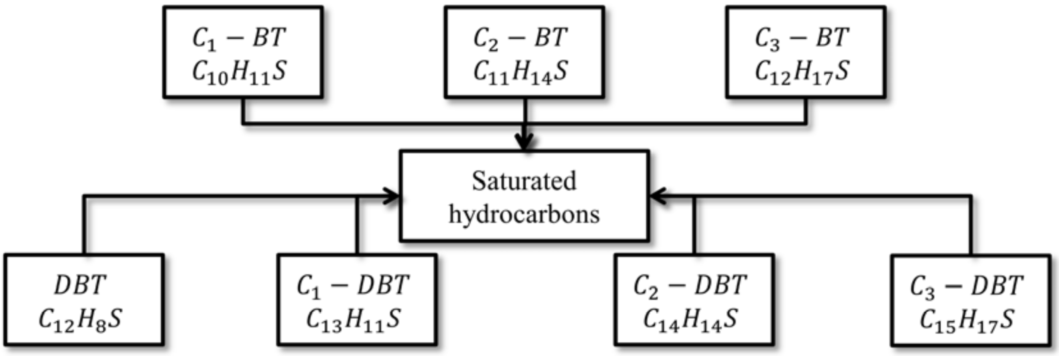

Fig. 1. Shortened kinetic scheme.

The developed mathematical model is based on the law of mass action and is represented by a system of differential equations that reflect the reactants concentrations change.

The industrial set “LG-24/7” was been the source for experimental data for the study. French catalyst HR-538 is used in this hydrotreatment set. The activity of the catalyst in respect of various SCC’s is already counted within the previously calculated effective rate constants.

The model used in the calculation of the rate constants for the conversion of individual sulfur components in the industrial set “LG-24/7”. The process of finding the kinetic parameters was performed by comparing the calculated sulfur content with the experimental total yield of sulfur using the method of least squares.

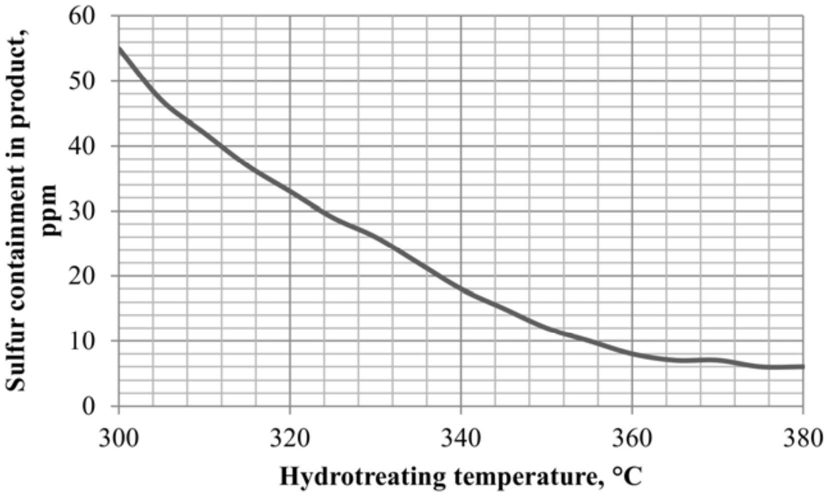

Fig. 2. Change of sulfur containment in hydrotreated product with the temperature rise

The relative error in the calculations, using data for the whole period of monitoring the installation not exceeded 5 %. Direct dependence of the rate constant transformation of SCC’s on the Gibbs energy change of the hydrogenolysis reaction is confirmed. Resullts of calculations show that residual sulfur content reaches a threshold value of 10 ppm even at 356 °C. Therefore, a further increase of temperature is not recommended because of the additional cost of heating the feed and of catalyst coking acceleration.

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SILICON-TUNGSTEN HETEROPOLY COMPOUNDS - THE ACTIVE CATALYST COMPONENTS OF INCOMPLETE OXIDATIVE CONVERSION OF C_1-C_2 ALKANES

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The combination of acid and redox properties is characteristic for heteropoly compounds (HPC). Numerous studies on use of HPC as catalysts of acid and redox type are known. Physico-chemical properties of W-HPC under conditions of the high temperature of catalysis and effect of reaction medium were insufficiently investigated. Therefore, identification of the nature of catalytic action of HPC in high temperature processes including oxidative conversion of hydrocarbons is difficult.

This paper presents experimental data on the study of thermal stability of $H_4SiW_{12}O_{40}\times nH_2O$ heteropoly acid (SiW-HPA) and its salts under the action of reaction medium at oxidative conversion of CH_4 or C_2H_6 at temperatures from 20 to 900 °C.

The initial structure of SiW-HPA was studied by temperature programmed reduction (TPR) and XRD methods. The nature of oxygen-containing fragments involved in the interaction with H_2 in TPR process by H_2 was determined.

Investigation of influence of steam-processing of HPA on its structural characteristics by IR spectroscopy, TPR, and XRD methods allowed to show that $H_4SiW_{12}O_{40}$ is characterized by 4 types of structural oxygen: W-O-W angled, W-O-W linear, W=O, Si-O-W. They are characterized by a.b. in the IR spectrum 790, 890 cm^{-1} (W-O-W, angled and linear, respectively) 980-1020 cm^{-1} (W=O), 930 cm^{-1} (Si-O-W), in XRD diffraction peaks in the area $2\theta = 5$-$20°$ (8-9°). 4 types of reactive oxygen species are observed in the TPR spectra. The first two of them belong to the reduction of the HPC structure. Molecular structure of HPA is stable in vapor-air medium in the temperature range of 20-400 °C. Changing in the secondary structure is observed at T > 400 °C due to dehydration. HPA destruction begins from 550 °C (TPR, IR, and XRD) from gradual destruction of structural fragments of heteropoly anion. However fragmentary formations (Si-O-W, W=O, in the IR spectra - a.b. 930 and 1020 cm^{-1}, respectively), probably are saved in the field of 650-900 °C at vapor-air processing. Partial preservation of the absorption bands, which are characteristic for HPA structure in IR spectra points to that. In parallel, with the preservation of structural fragments of the SiW-HPA there is a formation of oxide W phase (VI) of the tetragonal, and then orthorhombic coordination (apparently on the basis of fragments that have undergone destruction) in the presence of O_2 and water vapor at T = 650-900 °C.

Thus, it was installed that HPA preserves the secondary structure at the conditions of reaction medium for oxidative conversion of C_1-C_2 alkanes (hydrocarbons, air, water vapor) at 20-400 °C. At the temperatures $>$ 650 °C the oxide-similar W compounds are formed together with preserving the fragments of HPA structure.

Acknowledgements

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CONVERSION OF LIGHT ALKANES INTO OXYGENATES

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Results of research the activity of polyoxide catalysts containing 1, 5 and 10 % MoCrGa supported on natural carrier white clay (TWC) into oxidative conversion of propane-butane mixture into oxygenates are presented. The activity of developed catalysts (1 % MoCrGa/TWC, 5 % MoCrGa/TWC and 10 % MoCrGa/TWC) in oxidation of reaction mixture to acetaldehyde, acetone and methyl ethyl ketone was investigated by varying the temperature from 673 to 823 K and ratio of C_3-C_4 : O_2 : N_2 : Ar = 5 : 1 : 4 : 5; τ = 8 s and GHSV = 450 h^{-1}. Studies have been done on a flow-type installation at atmospheric pressure in quartz tubular reactor with fixed catalyst bed. Analysis of initial substances and reaction products was carried out using chromatographic method on «Agilent Technologies 6890N».

Acetaldehyde was not formed on the 1 % MoCrGa/TWC catalyst in the investigated temperature range. However, 33 % acetaldehyde is formed on the 5 % MoCrGa/TWC catalyst at 673 K, the number of which gradually decreases with increasing of reaction temperature up to 12 %. 36.5 % acetaldehyde is formed on the 10 % MoCrGa/TWC catalyst at 673 K. The formation of acetaldehyde reached 40 % while increasing the temperature to 723 K, and reduced to 33 % with a further increase in temperature.

Thus, 5 % and 10 % MoCrGa/TWC catalysts are optimal for the formation of acetaldehyde, on which is formed of 33 % and 36.5 % acetaldehyde at 673 K, respectively.

Change in activity of studied catalysts by the formation of acetone was determined. Yield of acetone at all temperatures also does not observe on 1 % MoCrGa/TWC catalyst. However, 33 % acetone is formed on 5 % MoCrGa/TWC catalyst at 673 K, the amount of which increased to 50.9 % with the growth of temperature. 37 % acetone is formed on 10 % MoCrGa/TWC catalyst at 673 K, but the number of acetone is reduced to a minimum with increasing temperature up to 823 K.

Thus, the 5 % MoCrGa/TWC is the optimal catalyst, on which the yield of acetone increased to 50.9 % at 673-823 K.

It was found that methyl ethyl ketone (MEK) is not formed on the 1 % MoCrGa/TWC catalyst in reaction mixture. However, 20 % MEK is formed on 5 % MoCrGa/TWC catalyst at 673 K, the amount of which increased to 38 % with the growth of temperature. 15 % MEK is formed on the 10 % MoCrGa/TWC catalyst at 673 K, but an inverse relationship in the formation of MEK is observed with increasing temperature up to 823 K, the amount of which is reduced.

Thus, 5 % MoCrGa/TWC catalyst is optimum for obtaining of 38 % MEK, 50.9 % acetone and 33 % acetaldehyde.

Developed active catalysts can be the basis for the creation of a pilot utilization process of C_3-C_4 hydrocarbons and production of oxygenates.

Acknowledgements

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OXIDATION OF LIGHT ALKANES TO HYDROGEN-CONTAINING COMPOSITIONS OVER SUPPORTED BLOCK CATALYSTS

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Tests of the ceramic block catalysts in oxidation of CH_4 were conducted in flow apparatus at atmospheric pressure in a quartz reactor with internal diameter of 0.025 m. The prepared catalyst block is wrapped in fiberglass and placed in a reactor. Initial reaction mixture was introduced at a rate of 50 ml/min after purging the system with inert gas (Ar) for 30 min at varying the ratio of reaction gases CH_4 and O_2 in a mixture from 1 : 1 to 4 : 1 and gradually increasing the temperature from 700 to 875 °C and volume rate from 1000 to 10000 h^{-1}.

The process of oxidative conversion of hydrocarbon mixtures which are close to real while gradually increasing the reaction temperature from 700 to 875 °C was investigated. Increase of methane conversion from 28 to 48 % is observed with the growth of temperature. The amount of the produced H_2 increases from 33 % to 84 % at 850 °C and again decreases to 70.2 % at 875 °C. A small amount of CO is formed at a temperature 700 °C which increases with increasing temperature from 0.6 to 40.5 %. Formation of C_2H_4 is observed at a reaction temperature 750 °C in an amount of 13.0 % and with the growth of temperature is lowered to 4 %. Thus, the temperature 850 °C is optimal for the formation of hydrogen, and 875 °C and 750 °C – for CO and C_2H_4, respectively. Effect of space velocity on direction of oxidative conversion of hydrocarbon mixture, which is close to the real, at variation of space velocity from 1000 to 10000 h^{-1} was studied. It was found that the hydrogen yield was 40.5 % at 1000 h^{-1}. Amount thereof increased to 84.0 % at 5000 h^{-1} and then reduced to 45.1 % with increasing space velocity up to 10,000 h^{-1}. The same dependence is observed for the formation of CO and ethylene. The amount of CO is increased from 10.5 % to 38.0 % and ethylene – from 7.8 % to 13.0 % at 5000 h^{-1}. Product yield gradually decreases with further increase in space velocity to 10000 h^{-1}. Increasing the space velocity from 1000 h^{-1} to 5000 h^{-1} positively affects on the conversion of initial mixture to desired products. 5000 h^{-1} is optimal space velocity for the formation of desired products. Thus, optimum ratios of main gases in the reaction mixture were also determined.

Thus, optimization of technological modes of oxidative conversion of hydrocarbon mixture was carried out. Effect of varying the reaction temperature, space velocity and ratio of gases for selective production of desired products was investigated. The temperature ranges of 725-875 °C and space velocity 5000 h^{-1} are optimal process parameters to produce hydrogen compositions. It is determined that the oxidative conversion of methane to hydrogen-containing mixture is carried out at the optimum ratio of components $CH_4 : O_2 = 2 : 1$ at a concentration of gases (50 % : 25 %), respectively.

Acknowledgements

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APPLICATION OF EXCILAMPS FOR DEGRADATION HERBICIDE 2,4-D BY USING FLOW REACTOR

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The effectiveness and content of phototransformation products of aqueous solutions of 2,4-dichlorophenoxyacetic acid (2,4-D) when exposed to UV radiation KrCl (λ ~ 222 nm) and Xe_2 (λ ~ 172 nm), excimer lamps have been studied. A flow-through photoreactor containing a KrCl and Xe_2 exciplex lamp has been used for the study of 2,4-D. The main products of phototransformation of herbicide were defined using HPLC and gas chromatography-mass spectrometry. The dynamics of H_2O_2 concentration depending on time and wavelength of radiation were studied. Toxicity assessment of aqueous solutions of 2,4-D after exposure was conducted. The stability of the obtained photoproducts for further biodegradation was also studied.

Fig. 1 shows the results of using the flow reactor based KrCl and Xe_2 excilamps. There are differences in efficiency. To increase the effectiveness of KrCl excilams possible by the addition of hydrogen peroxide (Fig. 2).

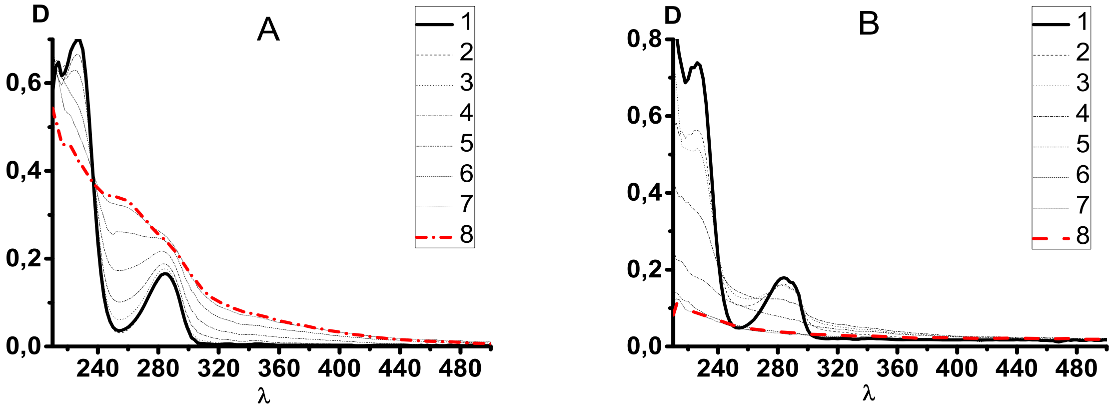

Fig. 1. (A) Absorption spectra 2,4-D (50 mg/l) in water (1), after radiation of KrCl (222 nm) 2 (2), 4 (3), 8 (4), 15 (5), 30 (6), 45 (7), 60 min (8); (B) Absorption spectra 2,4-D ($5 \cdot 10^{-5}$M) in water (1), after radiation of Xe_2 (172 nm) 2 (2), 4 (3), 8 (4), 15 (5), 30 (6), 45 (7), 60 min (8)

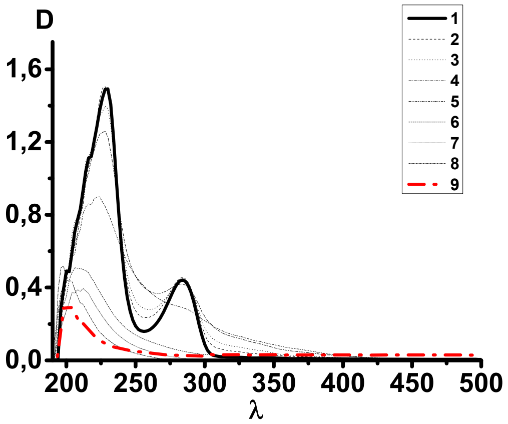

Fig. 2. Absorption spectra 2,4-D with addition of hydrogen peroxide (100 mg/l) in water (1), after irradiation of KrCl (222 nm) 2,5 (2), 5 (3), 10 (4), 20 (5), 40 (6), 60 (7), 90 (8), 120 min (9)

Acknowledgements

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THE TECHNOLOGY OF PREPARATION AND USE OF MICROSPHERIC MAGNETICALLY CONTROLLED ALUMINOSILICATE MATERIALS BASED ON CENOSPHERES OF ENERGETICAL ASH FOR THE IMMOBILIZATION AND SOLIDIFICATION OF RADIOACTIVE WASTE

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According to IAEA specifications liquid radioactive waste (LRW) are subject to a solidification [1]. Two processes on LRW immobilization in matrices on the basis of glass are implemented now. The installations on LRW immobilization into a borosilicate glass work in France and in Great Britain [2, 3]. The process of immobilisation of fraction Cs-Sr together with LRW of military origin in aluminophosphate glasses [4] is implanted in the Russia on FSUE “PA Mayak”. However, from the point of view of long-time environmental safety, glass matrices cannot be used for an immobilization of the waste containing long-living radionuclides. In works [5, 6] it is demonstrated that on the base of CHP cenospheres with certain proportion SiO_2/Al_2O_3 it is possible to create microspherical sorbents – precursors of mineral-like shapes of cesium and strontium radionuclides immobilisation with a possibility of crystallization of phases of the chosen structure type. However, it is necessary to notice that the selection of materials and technologies for reprocessing of radioactive waste (RAW) is defined by the safety level of all stages of treatment, safekeeping, transportation and dumping of waste. Thus the main role is played by such technical factors, as characteristics of RAW and gained finished product, reliability and a diapason of technology application, a degree of cutting of the RAW bulk and minimization of possible secondary wastes, economic purposiveness. The matrix materials meeting the indispensable demands do not exist currently.

An alternative approach to this problem can be based on the multifunctional glass-crystalline porous hollow materials based on cenospheres of fly energy ashes, which certain features appear on every stage of the multistage process of dealing with liquid RAW, for use of conditioning, immobilization and solidification of RAW. That said the thermal power fly ash microsphere components involvement in the process of RAW recycling simultaneously solves another actual problem of utilization of the fuel and energy complex waste.

The technique and technology of fractional separation of the aluminosilicate fly ahes of CHP in the upward flow of the dividing environment with imposition of the multiple pulsation and magnetic field of a certain intensity is developed by us. The cenospheres with stabilized chemical and mineral-phase and magnetic composition is received from the energy ashes from burning of the Ekibastuz (Kazakhstan) coals, including magnetic and aluminosilicate constituents of cenospheres. The band of cenospheres compositions, optimal for deriving of multifunctional porous materials is defined. Polyfunctional block porous materials with broad spectrum of action and powder microspherical porous materials that are oriented to a specific type of radionuclides and characterized by the regular porous structure with a double pore system, including interspheric and intraspheric voids is obtained on the basis of cenospheres with intended composition. Conditions of the water-soluble RAW transit into mineral water-insoluble forms due to solid-phase interaction of disperse radioactive oxides with a glass phase of matrix in a magnetic field and without him is developed.

The use of magnetocontrollable sorbents based on cenospheres of energy ashes for solidification of liquid RAW shall allow to concentrate RAW oxides in the volume of the matrix up to 30-40 wt %, to reduce the volume of liquid wastes from 5-20 times (porous matrix) up to 1500 times (sorbents), as well as to transfer liquid RAW to the stable mineral-like matrices (pollucite, Sr-feldspar, nepheline and their compositions) suitable for long-term dumping in geological formations, by means of the realization of energy-saving processes that do not require temperatures above 1100 °C. Involvement of affordable and renewable raw materials in the production of sorbents will reduce the costs of their production and reduce the amount of ash and slag waste in thermal power plants.

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THE TECHNOLOGY OF PRODUCING CARBON-MINERAL NANOSCALE MAGNETIC COMPOSITES AND THEIR USE IN THE HYDROGENOLYSIS PROCESS OF BROWN COAL INTO LIQUID HYDROCARBON PRODUCTS

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Macromolecules studied Kazakh coal consist of groups of condensed aromatic rings, the average for the middle stage of coal metamorphism in each group included about three rings. These groups are connected hydroaromatics and heteroaromatic structures that define a three-dimensional spatial location of the macromolecule. The volume of the open pores in the studied coals is as follows: volume (cm^3/g) with a diameter < 1.2 nm (micropores) is 0.02-0.07; when the diameter of 1.2-3 nm (mesopore) – 0.04-0.1, more than 30 nm (macropores) – 0.009-0.09. Total pore volume – 0.07-0.2 cm^3/g. When impregnating pulverized to 5-10 microns coal prepared magnetic fluids according to the method of synthesis of magnetite by chemical vapor deposition, using as dispersion medium and stabilizer of hydrocarbons with a boiling point of 350-380 °C, was obtained a magnetic composite, characterized by uniform distribution of magnetic material on the surface of the sorbent with a particle size of from 20 to 100 nm. Adsorption isotherm of coal impregnated with magnetic fluid, allows us to establish the mechanism of capillary sorption during the filling with fluid is the mesopores.

According to electron microscopy, in magnetic composites obtained by impregnating the magnetic fluid, the particles of magnetic material uniformly distributed on the surface of the coal. The greatest number of particles of the sorbent have a size of 20-100 Å. The specific surface area of brown coal decreases with impregnation of non-aqueous medium ~ 10 times. From the data on the saturation magnetization of the fitted linear dependence of the magnetization on the concentration of magnetic material.

The obtained magnetic composites tested in the process of hydrogenolysis of coal (Table 1).

Table 1. The results of the hydrogenation of coal in the presence of catalysts with different content of active phase in the atmosphere of synthesis gas.
The ratio of coal:pasteurisation 1:1,5; the pressure 5.0 MPa; the temperature of 410 °C

The composition of the active phase, %		Magnetization μs, the experimental	V_{gas}, %	The yield of liquid products, mass %				The remains, %	The loss, %
Fe_2O_3	CoO			80-180 °C	180-250 °C	250-320 °C	$\Sigma_{L.P.}$		
-	-	-	10,8	2,9	6,2	21,3	30,4	53,5	5,3
6,0	-	44,3	12,8	6,8	7,4	20,6	34,8	47,2	5,2
8,0	-	44,8	12,3	9,2	8,7	25,0	42,9	40,2	4,6
12,0	-	45,2	13,4	12,6	11,3	28,7	52,5	30,6	5,1
14,0	-	49,8	14,2	10,3	12,6	30,7	52,6	28,2	5,0
-	5,0	46,9	14,2	7,4	9,2	29,4	46,0	34,5	5,3
12,0	5,0	77,2	13,1	15,8	14,6	35,1	65,5	20,0	5,4

The results show that at a temperature of 410 °C, a pressure of 5.0 MPa with increasing concentration of Fe_3O_4 on the carrier from 6.0 to 12.0 mass. % yield of liquid products increases from 34.8 to 52.5 %. In the experiment without application of the active phase the yield of liquid products is of 30.4 %, and the addition of the active phases leads to an increase to 52.5 %. Introduction to the composition of the catalyst compound of cobalt leads to an increase in the yield of liquid products to 65.0 %. This increases the yield of gasoline fraction to 15.8 %.

It should be noted according to table 1, which is of great importance to the activity of the studied catalysts having the value of magnetization of the magnetic composites used, moreover, the higher magnetic properties of the catalyst the more active they are in the process of hydrogenation of coal.

THE CARBON DIOXIDE ACTIVATION TECHNOLOGY IN THE VORTEX ELECTROMAGNETIC FIELD IN THE PRESENCE OF MODIFIED MAGNETIC IRON-CONTAINING CATALYSTS

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Carbon dioxide represents almost inexhaustible source of natural carbon, CO replacement on CO_2 in catalytic synthesis of industrial yields is of special interest. CH_4, CH_3OH, C_2H_5OH, CO and light olefins and alkanes gained from CO_2. Higher hydrocarbons are not formed from CO_2 in distinction from CO.

Special properties of CO_2 molecule are conditioned by that it is the weak donor as the ionization potential is equal to 13,7 eV and is the strong acceptor in consequence of the significant electron affinity (2,9-3,8 eV). It can act as an acid, using lowest unoccupied molecular orbital (LUMO), or as the alkali, applying the n-unshared orbitals of oxygen. Charge cations for which one electrostatic interlinking has the great value, forms bond with an oxygen atom. Orbital complex formers create bonds with π-system of SO_2. They act as the bases. The reduction $CO_2 \rightarrow CO_2^{2-}$ and a metal oxidation happen under the action of π-dative electron transfer.

Carbon dioxide forms complexes with nucleophiles of OH^- type ($CO_2 + OH^- \rightarrow HCO_3^-$). The C-atom charged positively in consequence of high electronegativity of the O-atoms attacks the base.

The bonds in the coordination sphere of orbital d-metals at CO_2 are looses and the positive charge on the C-atom descends, therefore activated CO_2 molecule as distinct from the free molecule is more inclined to interreacting with orbital donors (H^-).

We have demonstrated that up to 75-80 % of ethanol is formed in the vortex electromagnetic reactor at magnetic field intensity in near-wall zone not less than 0,4T in the temperature interval of a working area 120-250 °C in the presence of water vapour and the modified iron-magnetic composites in the quality of catalyst.

Research have demonstrated that the oxidation-reduction reaction (1) is characteristic for ferrous contacts in the learnt conditions

$$Fe + H_2O \leftrightarrow FeO + H_2, \qquad (1)$$

and process proceeds further as CO_2 hydrogenation:

$$C_3H_8 + 6H_2O \xleftarrow[Ni,\ Co,\ Fe]{x\,=\,3,\,y\,=\,10} xCO_2 + yH_2 \xrightarrow[Fe]{x=2,y=6} C_2H_5OH + 3H_2O$$

More light hydrocarbons are obtained at CO_2 hydrogenation as distinct from CO because M–C bond which is the centre of chain growth, is formed not in the beginning of way, as at the CO hydrogenation, and in the middle of process as a result of aldehyde oxidative dissociation. The O-atom negative charge being a hindrance to the π-coordination which is indispensable for oxidative dissociation of a carbonyl group is enlarged whiles the alkyl radical growth.

The CO_2 hydrogenation process consists of typical stages of activation of H_2, CO_2, intraspheric reactions of type α- and β-shifts, oxidizing addition CR_2=O, decompounding of gem-diol compounds etc. Only key stages on which the process speed and direction depend are given below.

The temperature and rate of whole process depend on effectiveness of the catalyst in this reaction. Only $4d^{>5<10}$ and $5d^{>5<10}$-metals execute orbital rules at the H_2 homolysis. Therefore these metals activate H_2 at low temperatures, $3d^{>5<10}$-metals activate H_2 at average temperatures, and d^{10}-metals activate H_2 at high temperatures.

From orbit charts it is follows that *d*-metals carry out the adjoining of H-atom to C-atom of CO_2 without the symmetry rules violation. s-Metals realize this operation by means of the lone pair of oxygen which is perpendicularly to the reaction axis. Gem-alkoxide decompounding also happens easier on *d*-instead of on *s*-metals. The reaction of oxidative adjoining of aldehyde is specially difficult for *s*-metals, and on *d*-metals this stage happens without the symmetry rules violation. Oxidative dissociation of >C=O-group happens easier if it is adsorbed by π-bond, instead of the lone pair of O-atom. As the O-atom prefers a charge combination, that the carbonyl group on charge metals and oxides is coordinated by O-atom. π-Coordination of >C=O-function is carried out easier on orbit metals and at high temperatures. Therefore oxidative adjoining of >C=O-system happens on metals with the intermediate charge activity (Fe, Co, Ni).

Findings of orbital consideration of CO_2 hydrogenation reaction is qualitatively conformed with empirical data gained by us.

HYDROTHERMAL CARBONIZATION (HTC) OF ARGAN NUT SHELL FOR REMOVAL OF BISPHENOL-A

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Hydrothermal carbonization (HTC) of waste biomass, is a thermochemical conversion process to transform lignocellulosic biomass into value-added hydrochar. The hydrochar was prepared by hydrothermal carbonization from argan nut shell aiming at to be used in the removal of bisphenol A (BPA) from aqueous solution. The process parameters selected were temperature 180 °C (HTC-180) and 200 °C (HTC-200), and water to biomass ratio was fixed at 5:1 by weight %. Duration of the HTC processing was 6 h. Fourier transform infrared (FTIR), Total reflection X-ray fluorescence spectroscopy (TXRF), the Higher heating value (HHV), Nitrogen physisorption, thermogravimetric analyses (TGA) and Scanning electron microscopy (SEM) were performed to characterize the materials.

The influences of different adsorption parametres, such as solution pH (2-12), initial concentration (2 mg/L to 20 mg/L), and contact time (0 to 3 hours), were investigated in BPA removal. Adsorption Kinetics of HTC-180 and HTC-200 was described by the pseudo-second order model and adsorption isotherm was well defined by the Freundlich isotherm for HTC-180 and Langmuir model for HTC-200. The maximum multilayer and monolayer adsorption capacity of HTC-180 and HTC-200 for BPA was 200 mg/g and 301 mg/g respectively, at 25 °C, which demonstrates a great potential for the removal of organic molecule from aqueous solution. This study suggests that the hydrothermal carbonization is a very promising way to produce excellent adsorbents for wastewater treatment.

Keywords:

Hydrothermal carbonization; HTC; Hydrochar; Argan Nut Shell; Physical-chemical characterization; Adsorption; Bisphenol A; Langmuir; Freundlich

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HYDROFLUORINATION OF TETRACHLOROETHYLENE INTO PENTAFLUOROETHANE OVER A Cr–Al CATALYSTS: CATALYST COMPOSITION EFFECT, KINETIC STUDY

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In recent decades, considerable efforts have been focused on the synthesis of chladones, having zero ozone depletion potential. The most promising in this regard are chladones of the ethane row, namely, pentafluoroethane $CHF_2–CF_3$ (HFC-125), which is produced by the gas-phase catalytic hydrofluorination of tetrachloroethylene $Cl_2C=CCl_2$. A fluorination catalyst are based on amorphous Cr (III) compounds in combination with promoting and stabilizing admixtures of aluminum, magnesium, nickel, zinc and others [1,2].

The aim of the present work is study chromium-containing catalysts and the effect of adding promoters oxides Ni(II), Cu (II), Zn(II) and Co(III) on physicochemical and catalytic properties of the catalysts for the gas-phase hydrofluorination of tetrachloroethylene to pentafluoroethane (chladone HFC-125). Kinetic regularities of the reaction were also considered on a most active sample.

Catalysts were prepared by mixing of aqueous ammonia solution (9 %) and solutions chlorides of Me: Cr(III), Al(III), Ni(II), Cu(II), Zn(II), Co(III) at a constant pH 7.0 ± 0.5 and a temperature T = 70 ± 5 °C. After the completion of precipitation the suspension was aged for 1 h, washed with distilled water, filtered, dried in air at 110-120 °C for 12 h and calcined at 330-450 °C under nitrogen or air.

The thermal behavior of the samples in nitrogen and air in the temperature range 110-600 °C were studied by thermal and X-ray diffraction analyses, uv-vis diffuse reflectance spectroscopy, and specific surface and porous structure were measuremented.

The catalytic activity of samples in the fluorination of tetrachloroethylene to pentafluoroethane was determined using a flow reactor with a fixed catalyst bed (grain size of 0.25–0.5 mm) in the kinetically controlled region at 320-370 °C, 0.4 MPa, reactant molar ratios of HF : tetrachloroethylene = (10-20) : 1, and a residence time of 1–3 s. The activity was estimated in terms of the first-order reaction rate constant $k = -\ln(1-X)/\tau$, where X is the tetrachloroethylene conversion (in mole fractions) at the residence time τ.

It was found that additional promotion Cr-Al samples of nickel and copper increased the specific surface area of about 25-40 %. Moreover, the activity increased about 2 times. Modification of cobalt resulted in a decrease of the surface by 20 % and the activity decreased by about 2 times, while maintaining high selectivity.

On the basis of experimental data and the results of physical methods research the kinetic model of the process was suggest. The overall process includes a large number of possible reaction routes and, apart from its main products, might yield the products of side reactions like isomerization, elimination and disproportionation [3]. Based on the experimental data and results of mathematical modeling, the pathway of perchloroethylene hydrofluorination was identified. The process involves several consecutive reactions for the formation of main fluorination products and parallel reactions for the formation of by-products. The rate constants and activation energy of the PCE perchloroethylene conversion was obtained on the assumption of the first order of the reaction rate. Analysis of experimental data obtained on samples with different promoters testified that despite the difference in the activity and selectivity the pathway of the products formation is identical.

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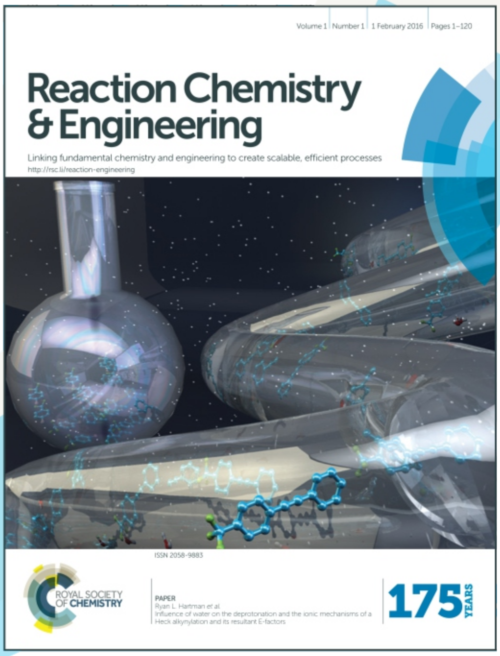

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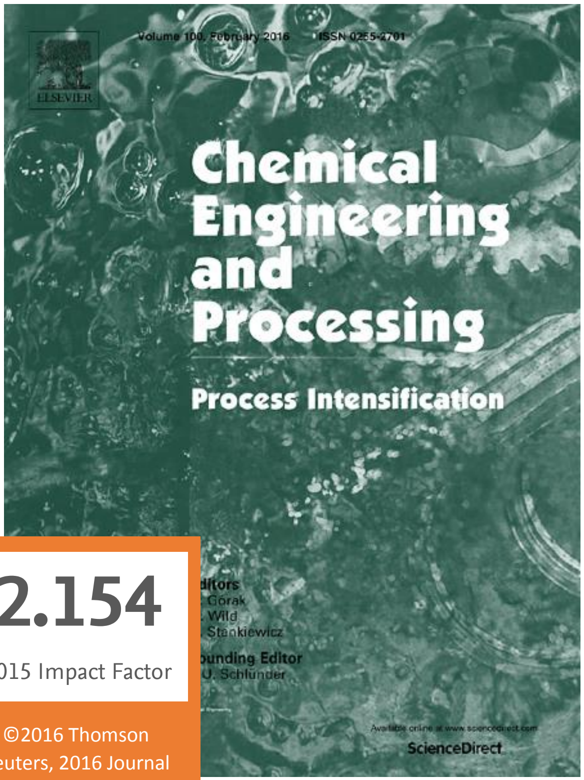

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